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SOME FLUORINE SUBSTITUTED TOLANES[1]

BY C. S. ROONEY[2] AND A. N. BOURNS

ABSTRACT

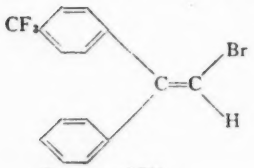
p-Trifluoromethyltolane and *p*-fluorotolane have been synthesized by the action of sodium or potassium amide in liquid ammonia on *para*-substituted 1,1-diphenyl-2-bromoethylenes. The geometrical isomers of 1-(*p*-trifluoromethylphenyl)-1-phenyl-2-bromoethylene have been separated and their configurations assigned on the basis of dipole moment measurements. *p*-Trifluoromethyltolane has been converted to a dibromide, which on oxidation gave benzoic and *p*-trifluoromethylbenzoic acids. Both tolanes have been reduced to the correspondingly substituted 1,2-diphenylethanes.

INTRODUCTION AND DISCUSSION

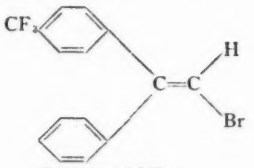
The syntheses and some reactions of (*p*-trifluoromethylphenyl)phenylacetylene (*p*-trifluoromethyltolane) (I) and (*p*-fluorophenyl)phenylacetylene (*p*-fluorotolane) (II) are described. These compounds were prepared in the course of some work which was to have been preliminary to a carbon-tracer investigation of the rearrangement of 1,1-diaryl-2-haloethylenes to tolanes in the presence of strong base (5, 6). A related investigation of this reaction, using a different system, was completed recently in another laboratory (4) and for this reason our mechanism studies were discontinued.

1-(*p*-Trifluoromethylphenyl)-1-phenylethylene (III) was prepared by the interaction of acetophenone and *p*-trifluoromethylphenylmagnesium bromide, as well as from *p*-trifluoromethylbenzophenone (IV) and methylmagnesium iodide. Compound IV was synthesized by the action of antimony trifluoride on *p*-trichloromethylbenzophenone at an elevated temperature. Bromination of III, followed by dehydrobromination, yielded 1-(*p*-trifluoromethylphenyl)-1-phenyl-2-bromoethylene (V), which, by a combination of elution chromatography on alumina and fractional crystallization at low temperatures, was separated into two geometrical isomers. On the basis of dipole moment measurements, the crystalline isomer (VA) was assigned the *cis* configuration, and the other (VB), a liquid at room temperature, the *trans* configuration. Isomer VB could not be obtained completely free of its higher-melting, less-soluble isomer.

[1]*Manuscript received July 18, 1955.*
Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario.
[2]*National Research Council Postdoctorate Fellow, Department of Chemistry, Hamilton College, McMaster University, 1952–1954.*



Compound VA



Compound VB

Compounds VA and VB on interaction with sodium or potassium amides in liquid ammonia solution both gave *p*-trifluoromethyltolane (I) in about 75% yield. Bromination of I yielded the dibromide VI, which on oxidation with chromic anhydride in acetic acid solution produced a mixture of benzoic and trifluoromethylbenzoic acids. Oxidation of I directly with potassium permanganate in acetone gave a low yield of these acids. Catalytic hydrogenation of compound I, using Raney nickel or Adam's catalyst at low pressure, produced 1-(*p*-trifluoromethylphenyl)-2-phenylethane (VII).

p-Fluorotolane (II) was prepared from 1-(*p*-fluorophenyl)-1-phenyl-2-bromoethylene (VIII) in a manner analogous to the synthesis of I. The bromo compound, VIII, prepared by the action of bromine on 1-(*p*-fluorophenyl)-1-phenylethylene, could not be crystallized, or separated into pure geometrical isomers by distillation or chromatography. Catalytic hydrogenation of II produced 1-(*p*-fluorophenyl)-2-phenylethane (IX).

EXPERIMENTAL*†

p-Trifluoromethylbenzophenone (*IV*)

p-Trichloromethylbenzophenone (10) (7.6 gm.) and 8.5 gm. of antimony trifluoride were mixed intimately and heated on a hot plate for 15 min. at a temperature sufficient to fuse the mixture. Water and benzene were added and 2.3 gm. of benzene-soluble material was isolated. Recrystallization from ethanol–water gave 1.53 gm., or 23% yield, melting at 116–118°C. Calc. for $C_{14}H_9OF_3$: C, 67.18; H, 3.63. Found: C, 67.24, 67.08; H, 3.75, 3.68.

1-(p-Trifluoromethylphenyl)-1-phenylethylene (*III*)

Method A

p-Bromobenzotrifluoride (9) (9.16 gm.) and 1.04 gm. of magnesium were allowed to react in 50 ml. of anhydrous diethyl ether. To the resulting red-colored Grignard reagent 4.88 gm. of acetophenone in 50 ml. of ether was added. The reaction mixture was worked up in the usual way. The resulting crude carbinol was dehydrated by heating at 150°C. in a nitrogen atmosphere for one and one-half hours. Distillation yielded 5.3 gm. of product (52.5% of theory), b.p. 78–79°C. at 0.1 mm., which crystallized. Recrystallization from methanol, or vacuum sublimation, gave the pure compound, m.p. 38–39°C.

**Melting points are corrected.*

†Carbon and hydrogen analyses were performed by Dr. F. G. Harcsar of McMaster University, and Miss G. Rotermann of the Dominion Rubber Company, Guelph, Ontario. Bromine analyses were carried out by the authors using the Carius combustion procedure.

Method B

p-Trifluoromethylbenzophenone (IV) (1.50 gm.) was added to an ether solution containing methylmagnesium iodide (0.22 gm. magnesium, 0.94 gm. methyl iodide) and the product was worked up as described under Method *A*. The yield of compound III, m.p. 38–39°C., was 1.12 gm. or 75% of theory. Calc. for $C_{15}H_{11}F_3$: C, 72.58; H, 4.47. Found: C, 71.82, 71.63; H, 4.98, 4.57.

Oxidation of compound III (0.068 gm.) with a solution containing 1.50 gm. of potassium permanganate, 10 ml. of acetone, and 7 ml. of water gave 0.043 gm. or a 76% yield of *p*-trifluoromethylbenzophenone.

1-(p-Trifluoromethylphenyl)-1-phenyl-2-bromoethylene (V)

Compound III (2.83 gm.) was brominated using bromine in acetic acid and the resulting dibromide dehydrobrominated by the procedure of Bergmann and Szmuszkowicz (2). On evaporation of the acetic acid solution, 3.78 gm., or 101% of theory, of a liquid product was isolated. After the product had been left overnight in the refrigerator, 1.54 gm. of crystalline solid (VA), m.p. 71–74°C., separated. This material was isolated by dissolving the surrounding liquid selectively in ethanol. The ethanol-soluble portion was chromatographed on an alumina* column using *n*-hexane as the developing solvent. A further 0.17 gm. of the solid isomer was obtained in this way, it being the last fraction removed from the column. Recrystallization of the combined solid product from ethanol gave pure VA, m.p. 74–75°C. The liquid fractions, which were eluted from the alumina column first, had n_D^{25} 1.5670–1.5690. When cooled to 0°C., or when cooled in ethanol solution to dry ice temperatures, these partially crystallized. Repeated chromatography, as well as fractional crystallization in ethanol solution, however, failed to give a sharply melting substance. What was probably the purest sample isolated had a melting point of 8–12°C., and n_D^{25} 1.5684. Anal. Calc. for $C_{15}H_{10}F_3Br$: C, 55.07; H, 3.08; Br, 24.4. Found: Solid isomer; C, 55.11, 55.11; H, 3.09; 3.07, Br, 25.9, 24.3. Liquid isomer; Br, 26.5, 24.8.

Dipole moment measurements determined using the resonance method (7) gave 3.46 D for the solid isomer (VA) and 2.26 D for the liquid product (VB). One therefore can assign with considerable certainty the *cis* (*p*-trifluoromethylphenyl and bromine *cis*) and *trans* configurations to the high- and low-melting isomers respectively. The moment of the liquid product was high for a pure compound of the *trans* configuration, indicating some contamination by the less soluble *cis* isomer.†

Oxidation of 0.072 gm. of compound VA in a solution containing 11 ml. of water, 15 ml. of acetone, 0.05 gm. of acetic acid, and 1.59 gm. of potassium permanganate yielded 0.045 gm. of *p*-trifluoromethylbenzophenone (81.5% yield).

**British Drug Houses chromatographic grade alumina, activated by heating for three hours with a Meeker burner, was used.*

†*It is of interest that a larger-than-expected moment has also been observed (1) for the trans isomer of 1-(p-bromophenyl)-1-phenyl-2-bromoethylene, although in this case the compound appears to be free of its geometrical isomer (4). This would suggest that our liquid product was purer trans isomer than the dipole moment might imply.*

p-Trifluoromethyltolane (*I*)

Compound VA, or VB, (0.61 gm.) in 15 ml. of diethyl ether was added to a liquid ammonia solution (70 ml.) containing 0.42 gm. of sodium amide. The mixture was evaporated to dryness after 15 min., 50 ml. of water added, and the insoluble product filtered. Recrystallization from ethanol–water, following vacuum sublimation, gave 0.135 gm., or 75% of theory, of the tolane melting at 104–105°C. Calc. for $C_{15}H_9F_3$: C, 73.17; H, 3.66. Found: C, 73.39, 73.38; H, 4.05, 4.02.

p-Trifluoromethyltolane Dibromide (*VI*)

To compound I (0.26 gm.), dissolved in 15 ml. of acetic acid, was added a slight excess of bromine in acetic acid and the solution heated at about 100°C. for 15 min. Following evaporation to 5 ml. and dilution with 20 ml. of water, 0.30 gm., or 72% of theory, of solid bromide was isolated, which after recrystallization from ethanol–water or isooctane melted at 159–161°C. Calc. for $C_{15}H_9F_3Br_2$: C, 44.30; H, 2.22; Br, 39.3. Found: C, 44.09, 43.86; H, 2.32, 2.22; Br, 37.0.

The dibromide VI (0.143 gm.) was added to a solution containing 0.40 gm. of chromic anhydride, 0.5 ml. of water, and 4 ml. of acetic acid. The mixture was heated at the boiling point for 15 min. and then 20 ml. of water was added. The precipitated solid (0.080 gm.) was filtered. A further 0.027 gm. was recovered from the filtrate by extraction with 60:40 benzene–ether. Extraction of the first product with 5% sodium hydroxide solution followed by acidification with dilute hydrochloric acid gave 0.046 gm. of acidic material. The combined solid products (0.073 gm.) were subjected to partition chromatography on a silicic acid column using methanol and isooctane as the stationary and mobile phases, respectively (8). The first compound removed from the column (0.038 gm.) melted at 218–220°C. and gave no depression when mixed with authentic *p*-trifluoromethylbenzoic acid. A later fraction gave 0.012 gm. of an acid whose melting point, 120–122°C., was unchanged in admixture with benzoic acid.

1-(p-Trifluoromethylphenyl)-2-phenylethane (*VII*)

Hydrogenation of compound I (1.33 gm.) in ethanol solution, using a Raney nickel catalyst at room temperature and 40 p.s.i., yielded 1.23 gm. of product (92% yield). Recrystallization from ethanol–water, or vacuum sublimation, gave the pure compound, m.p. 37.3–38.6°C. Calc. for $C_{15}H_{13}F_3$: C, 71.95; H, 5.23. Found: C, 71.77, 71.33; H, 5.15, 5.15.

1-(p-Fluorophenyl)-1-phenyl-2-bromoethylene (*VIII*)

This compound was prepared by bromination of 1-(*p*-fluorophenyl)-1-phenylethylene (X) (3) using the method of Bergmann and Szmuszkowicz (2). Compound X (21.2 gm.) gave 27.2 gm. (92% yield) of a product (VIII) boiling at 129–133°C. at 0.1 mm. Fractional distillation through a laboratory column *in vacuo* gave fractions with refractive indices varying from n_D^{25} 1.6131 to n_D^{25} 1.6162. Chromatography on an alumina column failed to give separation

into two distinct fractions. Calc. for $C_{14}H_{10}FBr$: C, 60.60; H, 3.61; Br, 28.8. Found: C, 59.97, 59.50; H, 3.59, 3.55; Br, 29.0, 28.4.

p-Fluorotolane (II)

Compound VIII (5.57 gm.) was added in ether solution to 100 ml. of liquid ammonia containing 2.5 gm. of potassium (as potassium amide) and the mixture was worked up as described for compound I. A crude solid (3.84 gm.) was isolated, which after recrystallization from ethanol–water weighed 3.01 gm. (75.5% yield) and melted at 109–110°C. Calc. for $C_{14}H_9F$: C, 85.71; H, 4.59. Found: C, 86.36, 86.29; H, 4.83, 4.68.

1-(p-Fluorophenyl)-2-phenylethane (IX)

Hydrogenation of compound II (0.128 gm.) with Raney nickel catalyst in ethanol solution at room temperature and 18 p.s.i. yielded 0.128 gm. of crude product, which after recrystallization from ethanol–water melted at 61–62.5°C. Calc. for $C_{14}H_{13}F$: C, 83.96; H, 6.50. Found: C, 83.16, 82.98; H, 6.49, 6.42.

ACKNOWLEDGMENT

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THE ACTION OF SULPHURIC ACID ON GLIADIN: WITH SPECIAL REFERENCE TO THE N-PEPTIDYL→O-PEPTIDYL BOND REARRANGEMENT[1]

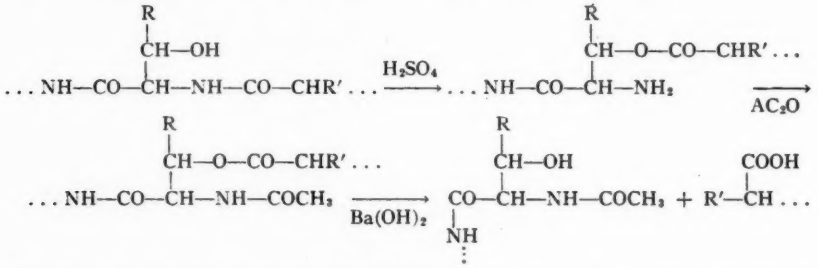
By L. K. Ramachandran[2] and W. B. McConnell

ABSTRACT

Treatment of gliadin with sulphuric acid transposes peptide bonds of serine from the amino to the hydroxyl group. Maximum transposition, 60–70% of the theoretical, occurs when the protein is treated with anhydrous sulphuric acid at 0°C. for 35 hr. No rearrangement was detected at threonine residues. Examination of the peptide material, obtained from the rearranged protein by Elliott's degradation method, indicates apparent "homogeneity". In an alternative scheme for the degradation, nitrous acid deamination of free amino groups was used. The resulting loss in serine content of the protein is direct evidence for the acyl migration of peptide bonds. Incorporation of sulphur and partial disappearance of several amino acids accompany the sulphuric acid treatment. The occurrence of these secondary reactions imposes limitations on the use of sulphuric acid as a reagent for the specific fission of peptide bonds.

INTRODUCTION

Attention has recently been directed towards methods which effect fragmentation of protein molecules in a predictable manner. Especially significant is Elliott's procedure for the cleavage of peptide bonds (7, 8, 9) at the amino groups of the β-hydroxyamino acids, serine and threonine. It is based on the strong acid-induced N-acyl→O-acyl transformations studied earlier by Bergmann, Brand, and Weinmann (2), Desnuelle and Casal (5), and Desnuelle and Bonjour (6), and is briefly outlined in the equations below:



This N-acyl→O-acyl migration might also occur where the ε-amino groups of δ-hydroxylysine (26) are linked in a peptide bond.

The treatment of silk fibroin with 97.5% sulphuric acid for three days at 20°C. (8) caused rearrangement in only 66% of the serine residues, the major N-terminal residue detected by the dinitrofluorobenzene method (24) being serine. The non-reactivity of the other serine residues was thought to result

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[2]*National Research Council of Canada Postdoctorate Fellow 1953–1955.*

from factors like steric hindrance. With lysozyme (9) nearly all the serine groups and a third of the threonine residues participated in the reaction. The non-dialyzability of the lysozyme derivative and the absence of the Ehrlich test for tryptophan suggested that cross linking occurred through those residues. Wiseblatt and McConnell (37), who applied the method to wheat gluten, also observed the preferential release of serine amino groups and suggested that the product was highly cross linked.

In the present study the action of anhydrous sulphuric acid in effecting bond transposition in gliadin has been studied from the quantitative aspects of time of reaction and temperature, to determine suitable conditions for further degradation studies on wheat proteins. The gliadin fraction was chosen because of its discrete characteristics. The reactivity of the liberated amino groups towards nitrous acid was determined. This treatment would convert the N-terminal serine residues to glyceric acid. After saponification of the O-acyl bond, the reactivity of the terminal dihydric alcohol towards periodic acid was studied. The above alterations in Elliott's scheme avoid the necessity for protecting the free amino N with a substituent often difficult to remove without other alterations to the material.

An effort has also been made to detect changes in some of the amino acids, arising from sulphuric acid treatment of the protein. Uchino (33) reported that silk fibroin was stable towards sulphuric acid at 7–8°C. for 11 days, but that later there was slow liberation of amino groups. Reitz *et al.* (28) noted that although appreciable hydrolysis of γ-globulin occurred in one week at room temperature there was only 2–3% hydrolysis in 10 days at 4°C. Work on wool (11) indicated considerable non-ionic combination of sulphate ions with the amino groups to form sulphamates. With other proteins (28) it seemed possible to account for all bound sulphate on the basis of ester formation with aliphatic hydroxyl groups, formation of sulphonic acids, and formation of thiosulphates by reaction with the sulphydryl groups. Although some workers observe very little destruction of tryptophan, cystine, and serine (28) other reports (20) indicate appreciable alteration besides the sulphamate formation. When wool was treated with sulphuric acid at low temperatures 10% of the serine and 25% of the arginine was lost. Phenylalanine and tyrosine showed a decrease which, as with tryptophan, may be partly accounted for by sulphonation of the benzene ring.

EXPERIMENTAL

Analytical Methods

Total N was determined by the micro-Kjeldahl method with mercuric oxide catalyst. ***Free amino groups*** were estimated by the Van Slyke nitrous acid method and a ninhydrin colorimetric procedure (31).

The difference in free amino groups before and after treatment of the materials with pH 9.1 borate buffer for 12–16 hr. was taken as a measure of the ***bond transposition*** (8).

Standard methods were employed for determination of the following: *amide N* (24), *cystine* (16), *methionine* (13), *arginine* (21), *tryptophan* (10). *Tyrosine* was determined by the 1,2-nitrosonaphthol reaction (25, 34).

Total S was estimated by a combined micro-combustion and volumetric method (32) and *formaldehyde* by the chromotropic acid color reaction (23). The method of Rice, Keller, and Kirschner (30) was used for the identification of the aldehydes as the 2,4-dinitrophenylhydrazones.

Treatment of Gliadin with Sulphuric Acid

One gram of gliadin (N—17.64%, prepared by the method of Blish and Sandstedt (3)) and 10 ml. anhydrous sulphuric acid (prepared by addition of the calculated amount of oleum to 97.5% sulphuric acid) were shaken together for the required time at the temperature desired. The reaction mixture was then poured with stirring into 20 times its volume of cold ether and the precipitated material washed repeatedly with ether. The material was dissolved in the minimum volume of 60% (v/v) ethanol, transferred to a Visking cellophane bag, and dialyzed exhaustively against distilled water. The contents of the bag were lyophilized. The recovery of the products was close to 97% based on nitrogen analyses.

Degradation of the Sulphuric Acid Treated Gliadin

The material obtained above was *acetylated* at pH 5.0 using acetic anhydride (8) or *formylated* with a mixture of formic acid and acetic anhydride (35). *Deacylation* was effected by means of anhydrous MeOH – HCl (1.5 *M* in regard to HCl) under conditions used by Boissonnas and Preitner (4). *Saponification* of the O-acyl bond was achieved using 0.01 *N* NaOH or 0.02 *N* $Ba(OH)_2$ (8).

Deamination of Sulphuric Acid Treated Gliadin

Two methods were employed. In the first, the reaction mixture was treated at 0.5°C. with solid $NaNO_2$ (1 gm. for every gram of protein), added in small portions during 20 min. In the other method 0.5 gm. of the material in 30 ml. 50% acetic acid was treated at room temperature with 1 gm. $NaNO_2$ added in small portions during 20 min. with agitation. The reaction mixtures were exhaustively dialyzed against distilled water and lyophilized. The latter method gave products free of color.

Reaction of Terminal Amino Groups with 1-Fluoro-2,4-dinitrobenzene (DNFB)

Conditions for the reaction and hydrolysis of the products for the release of the dinitrophenyl amino acids were those recommended by Porter (24). Separation of the 2,4-dinitrophenol and 2,4-dinitroaniline from the amino acid derivatives was effected on a chloroform – silicic acid column (19). The dinitrophenyl amino acids were identified by paper chromatography (22) and determined quantitatively by spectrophotometry at 360 mμ (24).

RESULTS

To establish a basis for assessing the results the serine content of gliadin was determined (27) and found to be 4.9% by weight. Gliadin, of molecular weight 30,000, on cleavage of all peptide bonds attached to serine N should therefore yield material containing about 15 fragments with an average chain length of 15–16 residues and with 0.65% amino N (3.7% of total N)

due to exposed serine amino groups. The original gliadin contained 1.01% of the total N as free amino N.

Figs. 1, 2, and 3 contain results obtained for total amino N, amino N arising from bond transposition alone, and amino N other than that arising from bond transposition when samples of gliadin were treated with H_2SO_4 at

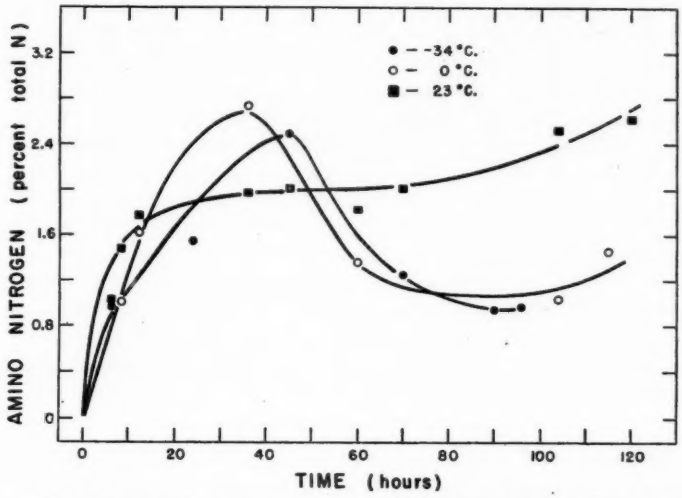


FIG. 1. Effect of time and temperature on free amino N released from gliadin by sulphuric acid.

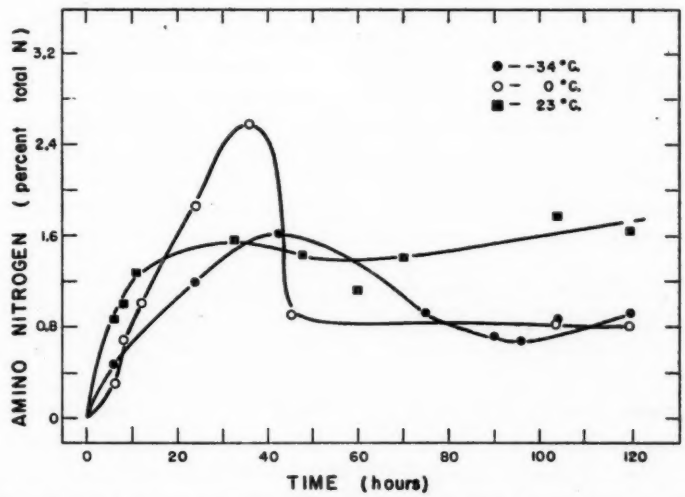


FIG. 2. Effect of time and temperature on the release of amino nitrogen by bond transposition alone during the sulphuric acid treatment of gliadin. Free amino nitrogen expected from a quantitative bond transposition at serine is 3.7% of total nitrogen.

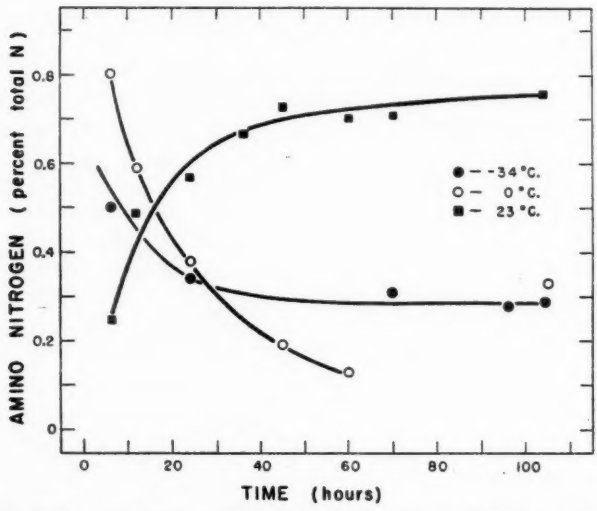


FIG. 3. Effect of time and temperature on amino nitrogen not arising from bond transposition during the sulphuric acid treatment of gliadin.

0°, 23°, and −34°C. for different lengths of time. The data were obtained on lyophilized products, isolated from the reaction mixtures, as described above.

The data indicate that in samples treated at 0°C. and −34°C. the total amino N increases during 35–45 hr. and thereafter falls to 50–65% of the maximum, remaining practically constant. At 23°C. amino groups increase rapidly for about 45 hr. after which there is a slow but continuous rise. Changes in amino N arising specifically from bond transposition follow the same pattern (Fig. 2). The pattern of changes in content of amino N other than those involved in the bond transposition is depicted in Fig. 3. In samples treated at −34° and 0°C. the values decrease gradually to a low value. Since the free amino N content of the original gliadin was measured to be 1.01% the initial decrease at 23°C. is relatively rapid but thereafter there is a progressive increase in free amino groups which may be the result of non-specific hydrolysis.

The difference between analytical values on duplicate preparations was of the order of 10%. The observed trends are therefore significant. The average deviation of the mean for determinations of amino N by the colorimetric method was ±1.5%.

Acylation and Saponification of the Treated Gliadin to Peptides

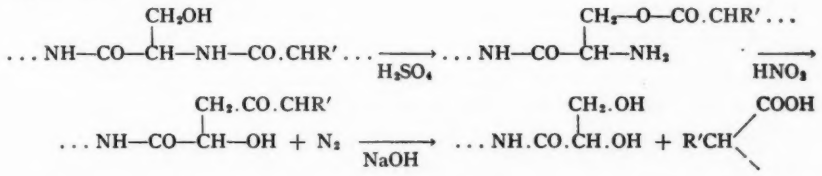
Two samples, one treated at 0°C. for 45 hr. and another treated at 23°C. for 60 hr. with sulphuric acid (0.312% and 0.221% of amino N, respectively, exposed by the bond shift), were subjected to acetylation, saponification, and deacetylation by methods referred to earlier. Material from saponification (after precipitation of barium either by passing in CO_2 at pH 6.5–7.0 or by

adding dilute sulphuric acid) had a high ash content which was retained even after the treatment with MeOH – HCl. To determine the serine end groups, the peptide samples obtained were oxidized with periodic acid. The amounts of formaldehyde obtained corresponded to 107.8 and 92.2% of the theoretical calculated from the amino N values for bond transposition.

The peptide samples were subjected to paper electrophoresis (Whatman 3 mm. 11×30 cm. sheet) using a pH 6.0 phthalate (0.05 *M*) buffer and 0.05 *N* acetic acid. The material was spotted along a line drawn across the middle of the sheet, which had been previously wetted with the electrolyte, and a potential of 220 v. was applied for a period of from two and one-half to three hours. No appreciable part of the material migrated toward either electrode so that although analyses indicated cleavage of the molecule at five to eight sites, no heterogeneity in the resulting material was demonstrable by paper electrophoresis. This observation is similar to results obtained in studies on gluten (37), where the suggestion was made that the material resulting from the treatments employed may consist of cross-linked polypeptide material of colloidal dimensions exhibiting marked homogeneity by physiochemical criteria. It was emphasized that the electrophoretic homogeneity may have resulted from polar groups introduced by the chemical treatments used. It thus appeared of some interest to avoid, at least, the steps of acylation and deacylation.

Deamination with Nitrous Acid and Saponification of the O-Peptide Bond

Some experiments were done therefore on deamination of the products from the sulphuric acid treatment. The reaction should convert the free amino groups to hydroxy groups and subsequent saponification should then yield a mixture of peptides with terminal glyceric acid. The reaction could be represented as follows:



Gliadin treated with sulphuric acid at 0°C. for 45 hr. was deaminated and saponified according to the above scheme of reactions. The isolated product was then oxidized with periodate (37) to determine terminal dihydric alcohols. Formaldehyde* equivalent to 105.5% of that calculated from bond transposition was recovered. The second method of deamination was applied to gliadin treated with sulphuric acid at 23°C. for 60 hr. The sample had a serine amino N value of 0.221% and total amino N 0.298%. After deamination the product had only 0.013% amino N, indicating destruction of 95.6% of the free amino

**Although the amounts of formaldehyde estimated in several samples examined were nearly equivalent to the bond transposition effected, the periodate consumed during the oxidation of the products was found to be several times higher than that expected. The sites in the protein-derivatives responsible for this reduction of periodate have not yet been determined.*

groups. Saponification with NaOH resulted in a product which on periodate oxidation yielded only a trace of periodate ammonia, indicating complete destruction of the serine amino groups. The formaldehyde produced during this oxidation corresponded to 112.8% of the calculated amount. The absence of acetaldehyde in the reaction mixture by the *p*-hydroxydiphenyl test indicated that no threonine residues were involved in the arrangement. This was confirmed when the aldehydes present were reacted with 2,4-dinitrophenylhydrazine and the hydrazones extracted and identified on paper chromatograms. Only one spot corresponding to formaldehyde was present.

The nitrous acid treated samples were hydrolyzed with 6 *N* HCl for 20 hr. as was a control sample of gliadin. The hydrolyzates were chromatographed in two dimensions (36) and the combined intensity of the ninhydrin spots due to serine and glycine was determined spectrophotometrically after extraction with 10% isopropanol. The values indicated that 80–90% of the serine determined as involved in the rearrangement had been destroyed by nitrous acid. However, application of both the dye test (17) and the biuret test (14) to electrophorograms of the two samples (deaminated H_2SO_4-treated gliadin, one at 0°C. for 45 hr. and the other at 23°C. for 60 hr.), prepared as described above, showed a single major component, which moved slowly towards the anode, but did not separate into differing fragments. Both the materials moved a distance of 2.3 cm. in three hours in 0.05 *N* acetic acid.

C-Terminal Groups of Degradation Products

Reaction of the degradation products with carboxypeptidase in a qualitative study indicated the following amino acids occupying C-terminal positions—tyrosine, "leucine",* valine, alanine, glutamic acid, and glycine. No amino acids were released when undegraded gliadin was treated with the enzyme, although application of the modified Schlack and Kumpf procedure (1) for C-terminal groups had indicated the presence of glutamic acid and "leucine" in less than molar amounts (unpublished results of the authors). It is thus possible that bond fission occurred at sites where serine is linked to the above amino acids.

Reaction of Exposed Amino Groups with DNFB

Gliadin was treated with sulphuric acid at 23°C. for four days, precipitated, acetylated, saponified, and then deacetylated with MeOH – HCl and the material fractionated roughly into MeOH – HCl soluble and insoluble fractions (37). The methanol insoluble sample (the amount of material recovered thus accounted for 25% of the nitrogen in the starting material) had very low amino N (0.137%) whereas the soluble fraction had a value of 0.490%. The free serine amino N was 0.082 and 0.183% respectively. The latter sample had a very high ash content and the formaldehyde values on periodate oxidation were abnormally high. It was considered desirable to determine the amount of free serine amino groups by condensing with DNFB and measuring the DNP-serine formed. The dinitrophenyl derivative was hydrolyzed and the DNP-amino acids in the ether extract and aqueous phase examined for their

*No differentiation has been made between leucine and isoleucine.

identity by paper chromatography (22) after initial purification on silicic acid (19). DNP-serine was found in the ether phase and the aqueous phase contained DNP-histidine. The presence of DNP-histidine is to be expected since histidine occupies the N-terminal position in gliadin (15, unpublished data of the authors). The DNP-serine amounted to 10.65 μM. while the amount theoretically expected from the other analyses was 12.59 μM. Although the recovery for serine amino groups thus appeared to be nearly quantitative, the condensation with the other free amino groups, known to be present from ninhydrin amino N analysis, could not be detected.

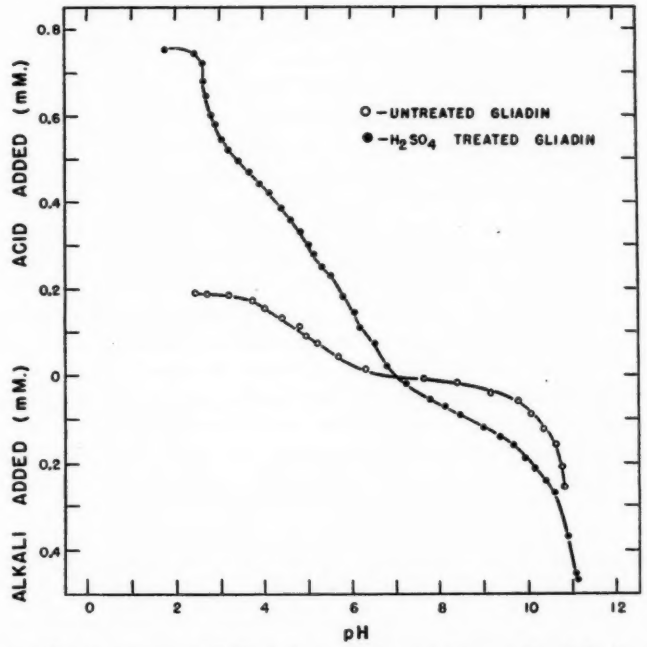


Fig. 4. Titration curve of gliadin before and after treatment with sulphuric acid.

The Effect of Sulphuric Acid Treatment on Some Amino Acid Residues

The titration curves of a sample of gliadin in 60% ethanol, before and after treatment with sulphuric acid at 23°C. for 70 hr., are indicated in Fig. 4. The shape of the curves suggests appreciable changes in the groups titrated in the pH region 2.5–8.5.

Table I contains the results of analyses for bound sulphate, amide N, arginine, methionine, and tyrosine. A single determination of tryptophan in the sample treated for 70 hr. at 23°C. indicated a decrease from 1.15 to 1.02%, of cystine from 2.35 to 1.85%, and of phenylalanine (12) from 5.45 to 4.72% on moisture and ash-free protein.

TABLE I

AMINO ACID CONTENT OF THE SULPHURIC ACID TREATED SAMPLES*

Reaction time, hr.	Reaction temp., °C.	Total S, %	Amide N, as % total N	Methionine	Arginine	Tyrosine
Untreated		0.943	25.6	1.53	4.52	3.5
6	23		23.3	1.11	3.83	2.49
24	23	2.32	23.91		3.67	1.97
70	23		19.75	0.971	3.84	0.71
120	23	3.24	18.69	0.71	3.40	0.65
6	0	1.62		0.75	3.57	2.27
60	0	2.17	25.63	0.67	3.62	0.95
104	0		22.92	0.55	3.41	
6	−34	1.05	20.74	1.22	3.66	2.94
90	−34	1.30	16.20	1.10	3.47	2.14
192	−34	2.40		0.98	2.79	2.29

**All values for amino acids as gm./100 gm. protein.*

DISCUSSION

The results presented show that time of treatment is a factor of importance in the sulphuric-acid-induced acyl migration of peptide bonds in gliadin. Although this study of transposition as a function of time indicates the best conditions (40 hr. at 0°C.), the complete migration of peptide bonds was not obtained under any of the conditions. The shape of the curves in Fig. 3 suggests partial disappearance of amino N during acid treatment at the two lower temperatures, whereas at 23°C. a non-specific hydrolytic cleavage appears to be superimposed. Amino groups might undergo reaction to form sulphamates (11, 29) or be involved in other reactions. If some of the newly formed amino groups participate in such reactions under the conditions of treatment used, it would be impossible to detect or make use of a complete shift of the peptide bonds. Apparent incompleteness in the shift cannot be explained solely on the basis of factors like reactivity of the residues in the protein molecule. Elliott (9) suggested the occurrence of polymerization reactions involving tryptophan residues in the case of lysozyme, but quantitative fission at serine groups and at a third of the threonine residues had occurred. In silk fibroin the cleavage at serine residues was of the order of 66% (8). In gliadin the maximum observed is of the same order (Fig. 2). Thus the effective cleavage of these bonds seems to vary with different proteins.

The present observations indicate that problems arising in the blocking of amino groups and removal of the blocking agent later could be avoided by deamination and that, with gliadin, the removal of the amino groups by nitrous acid is quantitative. This treatment would however convert terminal serine residues to glyceric acid. In theory, this simplification in procedure could distinguish between serine residues rearranged in the first step and those encountered later. Samples of treated protein deaminated in this way showed a decrease in content of serine in the hydrolyzate, of the same order as involved in the bond rearrangement. This in effect constitutes direct evidence of a shift of peptide bonds attached to the serine N in gliadin. Desnuelle (see Ref. 9, p. 140) however has encountered difficulty with some proteins in dimethylating or deaminating the amino groups exposed by sulphuric acid.

The results obtained indicate the incorporation of considerable amounts of undetermined forms of sulphur into the protein during the treatment with acid. Extensive chemical modification of the original protein is also shown by the changes in the content of amide bonds, methionine (cf. 18), arginine, tyrosine, cystine, and phenylalanine. The tryptophan reaction was still strong in some of the products examined. Side reactions involving free amino groups in the sulphuric acid medium are indicated by the gradual diminution of non-serine amino N with time. This perhaps involves, amongst other possibilities, sulphamate formation. The differences observed in the titration curves of gliadin, before and after treatment, possibly result from rather extensive alterations.

The incomplete nature of the rearrangement and the chemical modification of several of the constituent amino acids in the protein severely limit the scope and usefulness of sulphuric acid as a reagent for the selective fission of peptide bonds. The results presented herein do nevertheless provide direct evidence for strong acid-induced acyl migration in gliadin and indicate that a fairly specific cleavage of peptide bonds can thereby be obtained. More satisfactory schemes for selective protein hydrolysis will probably be developed in the future but, for the present, degradation based upon the sulphuric-acid-induced bond transposition remains a useful tool in the study of proteins. Improved understanding of the various effects of sulphuric acid on proteins will lead to rational applications of the procedure and facilitate interpretation of the results.

ACKNOWLEDGMENT

The authors are indebted to Mr. J. A. Baignee for determinations of sulphur.

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THE REACTION OF ACTIVE NITROGEN WITH AZOMETHANE[1]

By D. A. Armstrong[2] and C. A. Winkler

ABSTRACT

The main products of the reaction between active nitrogen and azomethane were hydrogen cyanide and ethane. Traces of methane, ethylene, and acetylene were also formed, together with small amounts of an unstable product. Activation energies of about 0.5 ± 0.4 and 1.9 ± 0.3 kcal. per mole, with corresponding steric factors of 10^{-1} to 10^{-3} and 10^{-3} to 10^{-4}, were estimated for the reactions of active nitrogen with methyl radicals and azomethane respectively, on the assumption that atomic nitrogen is the reactive component of active nitrogen. Azomethane appeared to catalyze the deactivation of active nitrogen.

INTRODUCTION

Free alkyl radicals have been postulated as intermediates in many of the hydrocarbon – active nitrogen reactions studied in this laboratory, and it has been invariably assumed that they were very rapidly destroyed by reaction with active nitrogen. The present study represents an attempt to evaluate experimentally the kinetic characteristics of the methyl radical – active nitrogen reaction.

EXPERIMENTAL

The apparatus and analytical methods have been described in earlier papers (4). Two concentrations of active nitrogen, which differed by a factor of approximately ten, were used. For the higher concentration, molecular nitrogen at a flow rate of 9.75×10^{-5} mole/sec. was admitted to the condensed discharge. The lower concentration was obtained by reducing the flow of nitrogen to 3.53×10^{-6} mole/sec., while the pressure in the system was maintained at the previous value (*ca.* 1.0 mm.) by introducing argon into the discharge tube at a flow rate of 7.28×10^{-5} mole/sec. In two experiments on the hydrogen atom – azomethane reaction, a comparable hydrogen–argon mixture was passed through the discharge tube.

Three samples of azomethane were prepared from dimethylhydrazine by the method of Leitch* (11); these showed identical vapor pressure – temperature relations.

Reaction temperatures were measured with two copper–constantan thermocouples. One of these was situated directly below the hydrocarbon inlet tube in the center of the reaction vessel, while the other was located near the top of the vessel at the active nitrogen inlet.

[1]*Manuscript received July 22, 1955.*
Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the Consolidated Mining and Smelting Co., Trail, B.C., and the National Research Council of Canada.
[2]*Holder of a National Research Council Studentship, 1953–1954, and a Cominco Fellowship, 1954–1955.*
**The authors are grateful to Dr. L. C. Leitch of the National Research Council, Ottawa, for one sample of azomethane and for some of the dimethylhydrazine. Further supply of the latter was obtained from Brickman and Company of Montreal.*

RESULTS

A preliminary experiment with azomethane mixed with molecular nitrogen in approximately the proportions used in the subsequent studies of the active nitrogen reaction showed no significant thermal decomposition of azomethane under these flow conditions at 400°C. Also no decomposition was observed when argon alone was passed through the discharge tube and allowed to mix with azomethane in the reaction vessel.

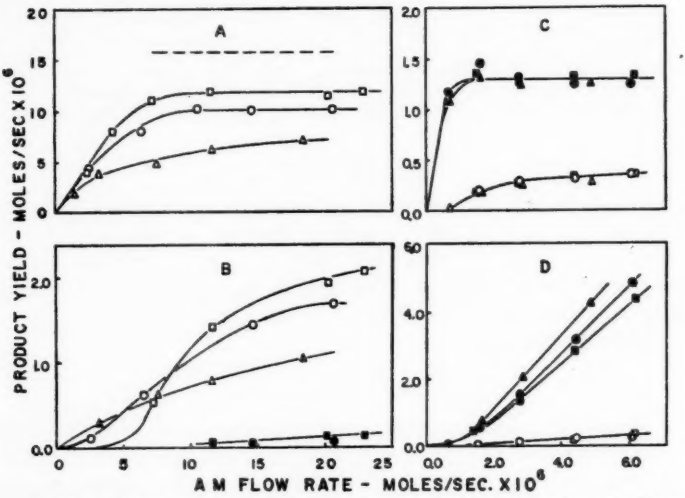

FIG. 1. Relations between flow rate of azomethane and yields of products in the reaction between azomethane and active nitrogen.

A: HCN production at high active nitrogen concentration:

HCN	Temp. (°C.)
□	390
○	160
△	85

B: Production of C_2 hydrocarbons at high active nitrogen concentration:

C_2H_6	C_2H_4	Temp. (°C.)
□	■	390
○	●	160
△		85

C: Production of HCN and C_2 hydrocarbons at low active nitrogen concentration:

HCN	C_2H_6	Temp. (°C.)
■	□	400
●	○	180
▲	△	50

D: Production of the unstable product and azomethane recovery at low active nitrogen concentration:

Recovered AM	Unstable product	Temp. (°C.)
■	□	400
●	○	180
▲		50

The condensable products of the active nitrogen – azomethane reaction consisted mainly of hydrogen cyanide and ethane. Unreacted azomethane was also recovered. A Le Roy still (10) was used to separate the ethane fraction, which was subsequently analyzed with a mass spectrometer.*

The HCN content of the remaining fraction was estimated by absorption in KOH solution and titration with standard $AgNO_3$ solution (9). Unreacted azomethane was obtained by difference. The yields of HCN and C_2 hydrocarbons for three different temperatures, at each of the active nitrogen flow rates used, are shown in Fig. 1A, B, and C.

Analysis of the uncondensed gases from two experiments at the higher active nitrogen flow rate indicated that methane was produced only in small amounts in the azomethane – active nitrogen reaction and that the hydrogen production approximated to the HCN yield.

In all of the active nitrogen – azomethane experiments small amounts of methane and nitrogen (in roughly equal proportions as determined by mass spectrometer analysis of several samples) were evolved when the condensable products were evaporated from one vessel to another, and also during distillation in the Le Roy still. The evolution of these gases in the same proportion was also observed from the products of the two experiments with the hydrogen atom – azomethane reaction. These observations indicate that the formation of an unstable product in the active nitrogen – azomethane reaction is a result of secondary hydrogen atom – azomethane reactions. From the total amounts of methane and nitrogen formed by complete decomposition of the unstable product, it was possible to estimate its yield on the assumption that one molecule of the unstable material decomposed to one molecule of methane and one molecule of nitrogen. The data obtained from such estimates, together with the recovery of azomethane, have been plotted in Fig. 1D as a function of the azomethane flow rate for a number of experiments at the lower active nitrogen flow rate.

No products other than residual azomethane and hydrogen cyanide were detected in significant amounts by mass spectrometric analysis of the final fraction from two experiments at 45° and 177°C. with the lower active nitrogen concentration. The hydrogen cyanide yields calculated from these analyses agreed with those obtained by the chemical method mentioned previously.

At the lower temperatures material balances were within a few per cent of the theoretical. However, at higher temperatures the material balances were between 88 and 100% and some polymer formation was observed.

Experiments with ethylene and propylene at high temperatures and high flow rates, such that consumption of the active nitrogen should be complete (4), indicated a value of about $1.60 \pm 0.10 \times 10^{-5}$ mole/sec. for the higher active nitrogen flow rate (dotted line, Fig. 1A). Similar experiments with ethane and ethylene gave a value of $1.31 \pm 0.06 \times 10^{-6}$ mole/sec. for the lower flow rate.

Apart from the unstable product, the hydrogen atom – azomethane experiments yielded large quantities of ethane and a higher boiling fraction. Material

*The authors are indebted to Dr. H. I. Schiff of this department for the mass spectrometer analyses.

balances, calculated on the assumption that the latter fraction was residual azomethane or dimethylhydrazine, were well over 100%, a feature in which the hydrogen atom – azomethane experiments differed from those with active nitrogen.

DISCUSSION

Although evidence has recently been obtained (3) to indicate the presence of more than one reactive species in active nitrogen, the identities of the species have not been established. As in most of the previous studies, therefore, the present results will be discussed on the assumption that atomic nitrogen is the only reactive species involved.

At the lower active nitrogen concentration the hydrogen cyanide production increased rapidly with azomethane flow rate, and attained a constant maximum value which was virtually independent of temperature. The close agreement between this maximum hydrogen cyanide yield and the corresponding yields from ethane and ethylene suggests that the hydrogen cyanide production from azomethane represents the complete consumption of the relatively small amount of active nitrogen available in these experiments.

On the other hand, the hydrogen cyanide production from azomethane at the higher active nitrogen flow rate never approached the value obtained with ethylene and propylene, although the constant yield observed for higher azomethane flow rates would again imply complete consumption of the available active nitrogen at 160° and 400°C.

The apparent loss of active nitrogen in the presence of azomethane might be due to catalyzed recombination of nitrogen atoms with azomethane as a third body; thus:

$$N+N+CH_3{-}N{=}N{-}CH_3 \rightarrow N_2+CH_3{-}N{=}\dot{N}{-}CH_3{}^*. \qquad [1a]$$

This would be in competition with the reaction:

$$N+CH_3{-}N{=}N{-}CH_3 \rightarrow HCN+N_2+H_2+CH_3 \qquad [1b]$$

which appears to be the most reasonable process for the initial nitrogen atom attack on azomethane.

Both of these reactions are first order in respect of azomethane. A competition between them would thus explain the constant hydrogen cyanide production observed at azomethane flow rates in excess of the critical flow rate. A difference in activation energy would explain the increase in hydrogen cyanide production with temperature. Also, since the recombination reaction is second order in respect of the nitrogen atom concentration, a significant reduction in the concentration of this reactant should favor conversion of the active nitrogen to hydrogen cyanide, and the apparent difference in behavior at high and low active nitrogen concentrations can be explained.

It might be noted parenthetically that if excited or metastable nitrogen molecules, rather than atoms, were the major component of active nitrogen it would be difficult to account for this behavior, which has also been observed with other compounds (1, 2).*

**It is hoped that a general discussion of the behavior may be published shortly.*

Methyl radicals formed in the initial process may react with nitrogen atoms as follows:

$$N+CH_3 \rightarrow HCN+2H \qquad [2a]$$

$$\rightarrow HCN+H_2 \qquad [2b]$$

$$\rightarrow CN+H_2+H. \qquad [2c]$$

Reaction [2*c*] is probably slightly endothermic; moreover if it were extensive, cyanogen might have been expected as a significant product. Although reaction [2*a*] is thermodynamically less favorable than [2*b*], it permits conservation of spin (1), while [2*b*] does not.

Ethane formation presumably occurred by the reaction:

$$CH_3+CH_3+M \rightarrow C_2H_6 \qquad [3]$$

which seems to have a negligible activation energy and a steric factor close to unity (12).

Methane, ethylene, and acetylene are all minor products and were probably produced in relatively unimportant processes (for example methane might have been formed in reactions involving hydrogen abstraction by methyl radicals).

From the results of the present investigation and from previous studies of the hydrogen atom – azomethane reaction (5) it would seem that secondary hydrogen atom – azomethane reactions must have been relatively insignificant in the reaction of active nitrogen with azomethane. However, formation of the unstable product implies that a small concentration of atomic hydrogen was present in the system. This may be taken as evidence for the occurrence of reaction [2*a*]. Indeed it is possible to infer from the relative proportions of HCN, C_2H_6, and the unstable product that this reaction largely predominated over reaction [2*b*].

The chain characteristics observed in previous studies of the hydrogen atom – azomethane (5) indicated that hydrogen atom – azomethane complexes might be relatively stable. Since such complexes might decompose to yield methane and nitrogen in roughly equal proportions (and possibly other products which are condensable in liquid nitrogen) they might well be identical with the unstable product recovered in the present investigation.

By making certain simplifying assumptions it is possible to obtain estimates for the activation energies of reactions [1*b*] and [2] from the results of the experiments at the lower active nitrogen concentration where the occurrence of reaction [1*a*] could be neglected.

On the basis of the mechanism already outlined the equations required for these calculations may be formulated as follows:

$$N+AM \xrightarrow{k_1} HCN+H_2+N_2+CH_3 \qquad [1b]$$

$$N+CH_3 \xrightarrow{k_2} HCN+2H \text{ (or } H_2) \qquad [2]$$

$$CH_3+CH_3 \xrightarrow{k_3} C_2H_6 \qquad [3]$$

$$d(\mathrm{HCN})/dt = k_1(\mathrm{AM})(\mathrm{N}) + k_2(\mathrm{Me})(\mathrm{N}) = R_1$$

$$d(\mathrm{Me})/dt = k_1(\mathrm{AM})(\mathrm{N}) - k_2(\mathrm{Me})(\mathrm{N}) - k_3(\mathrm{Me})^2$$

$$d(\mathrm{C_2H_6})/dt = \tfrac{1}{2}k_3(\mathrm{Me})^2 = R_2.$$

The usual steady state approximation for the methyl radical concentration gives:

$$\frac{k_2}{k_3^{\frac{1}{2}}} = \frac{(Q_1 - 2Q_2)}{2^{3/2} \cdot F_n \cdot Q_2^{\frac{1}{2}}} \times \frac{RT}{pV^{\frac{1}{2}}} \times (\text{total molar flow rate}) \qquad [\text{i}]$$

$$\frac{k_1 \cdot k_3^{\frac{1}{2}}}{k_2} = \frac{2^{\frac{1}{2}} \cdot (Q_1 + 2Q_2)}{(Q_1 - 2Q_2)} \times \frac{Q_2^{\frac{1}{2}}}{F_a} \times \frac{RT}{pV^{\frac{1}{2}}} \times (\text{total molar flow rate}) \qquad [\text{ii}]$$

$$k_1 = \frac{(Q_1 + 2Q_2)}{2 \cdot F_n \cdot F_a} \times \left(\frac{RT}{pV^{\frac{1}{2}}}\right)^2 \times (\text{total molar flow rate})^2 \qquad [\text{iii}]$$

F_a and F_n are the flow rates of azomethane and nitrogen atoms in the reaction zone, and Q_1 and Q_2 are the observed rates of production of hydrogen cyanide and ethane respectively.

Calculations were made for the higher azomethane flow rates, where the reaction flame was confined to the upper part of the reaction vessel and the reading of the upper thermocouple could be assumed to indicate the reaction temperature. With the assumption of completely turbulent flow in the reaction zone, F_a and F_n may be assigned steady-state values. As a rough approximation the values of F_a and F_n in the reaction zone were assumed to be equal and independent of temperature. A value of 1.30×10^{-6} mole/sec. (equal to the average hydrogen cyanide production) was therefore taken to represent both F_n and F_a.

The reaction volume V was assumed to remain constant over the temperature range studied and was estimated from the dimensions of the reaction flame to be about 50 cm^3. It was also necessary to assume negligible ethane consumption by the reaction:

$$\mathrm{N} + \mathrm{C_2H_6} \rightarrow \mathrm{HCN} + \mathrm{CH_3} + \mathrm{H_2}.$$

Collision diameters of 3.0, 3.5, and 5.5 Å for nitrogen atoms (4), methyl radicals (6), and azomethane (8) respectively were used in the calculation of the collision numbers and estimation of the steric factors.

The ratios $k_2/k_3^{\frac{1}{2}}$ calculated for the three different temperatures gave a value of 0.5 ± 0.4 kcal. per mole for $E_2 - \frac{1}{2}E_3$ and the ratio $P_2/P_3^{\frac{1}{2}}$ was found to be between 10^{-1} and 10^{-2}. Allowing for the possible decreases in P_3 at low pressures (7) a lower limit of 10^{-3} may be set for P_2. If secondary hydrogen atom – azomethane reactions, which led to the formation of methyl radicals or ethane, were responsible for some of the decomposition of the azomethane, the fraction of hydrogen cyanide formed in the methyl radical – active nitrogen reaction would be greater than indicated and the ratios $k_2/k_3^{\frac{1}{2}}$ and $P_2/P_3^{\frac{1}{2}}$ would be correspondingly greater. The values of the ratios $k_2/k_3^{\frac{1}{2}}$ and $P_2/P_3^{\frac{1}{2}}$ calculated above can thus be regarded as lower limits.

A value of 2.0 ± 0.3 kcal. with a corresponding steric factor between 10^{-2} and 10^{-4} was estimated for E_1 from the values of k_1 calculated by equation [iii] for the three temperatures. Relation [ii], which is independent of F_n, gave a value of 1.4 ± 0.3 kcal. for $E_1-E_2+\frac{1}{2}E_3$. This is consistent with the values of 2.0 ± 0.3 and 0.5 ± 0.4 kcal. per mole calculated for E_1 and $E_2-\frac{1}{2}E_3$ with the other two relations. These calculations indicate that the reaction of nitrogen atoms with azomethane was far more rapid than their reaction with saturated hydrocarbons and comparable in rate with their attack on unsaturated hydrocarbons.

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DISINTEGRATION-RATE DETERMINATION BY 4π-COUNTING

PART III. ABSORPTION AND SCATTERING OF β RADIATION[1]

By B. D. Pate[2] and L. Yaffe

ABSTRACT

The "coincident discharges" in a 4π-counter have been examined and found to be due in the main to gas and wall back-scattering. This can be resolved into two components—scattering near to and far from the source. Curves have been obtained for the back-scattering of β radiation by the source-mounting film and for the absorption of the incident and back-scattered radiation. Back-scattering by the film is shown to be great enough to introduce a large error into the "sandwich" method which is currently in use for correcting for source-mount absorption.

INTRODUCTION

Previous publications in this series (37, 38, 39) have described experimental work aimed at improving the accuracy of absolute counting using a 4π-counter. In this paper additional experimental data are presented, which enable identification to be made of the agency giving rise to the discharges occurring coincidently in both half-counters, and examination to be effected of some of the scattering and absorption processes involved in using a 4π steradian geometrical arrangement.

The penetration of electronic radiation through matter is a complex phenomenon owing to the variety of processes by which interaction may occur (5). With an initially collimated beam of monoenergetic electrons, interaction with a layer of material up to a superficial density of a few hundred μgm./cm.^{2} occurs by means of a few scattering events per electron. This results in the beam spreading without too great an energy or intensity loss. With thicker layers, more scattering events per electron occur and a transition to "multiple scattering" takes place. With still thicker layers the electrons no longer have a preferred direction of motion and the process resembles diffusion. The number of electrons now emerging from the foil decreases with increasing foil thickness, i.e. absorption of the radiation occurs.

The single scattering of electrons has been treated theoretically (2, 33) and the multiple scattering has been treated in an approximate way (4). When the system is further complicated by an uncollimated β radiation with a continuous energy spectrum, a theoretical analysis is very difficult. Consequently the absorption and scattering of β radiation have only been described empirically, principally with counting geometries of less than 2π steradians.

The absorption process, of interest both as a source of error in disintegration-rate measurements and as an energy determination method, has been the subject of a voluminous literature (6, 17, 19, 20, 21, 27, 29, 41, 42). Our knowledge

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Contribution from the Radiochemistry Laboratory, Department of Chemistry, McGill University, Montreal, Quebec, with financial assistance from the National Research Council of Canada and Atomic Energy of Canada Ltd.
[2]*Holder of a National Research Council Studentship.*

of the back-scattering of β radiation is largely due to experimental work performed in connection with disintegration-rate determinations using $\ll 2\pi$ geometry systems (12, 16, 22, 26, 50, 51).

Absorption measurements in a 4π-counting geometry are of interest for two reasons. First, the effects observed are due to absorption alone, and scattering effects which cause complications like maxima in absorption curves (15, 18, 34, 45) are virtually absent. Secondly, measurements in the absorber thickness range below a few hundred μgm./cm.^{2} (not hitherto reported), particularly with sources with minimal self-absorption, will provide absorption data regarding the lowest energy electrons in the β spectrum. The results given in an earlier paper in this series (39) and those of Suzor and Charpak (47, 48) indicate large absorption effects in this region.

Prior to the present investigation no detailed study of absorption effects in a 4π-counter has been reported. Measurements of the variation of total counter, half-counter, and coincidence counting rates have previously been made (25, 44, 47, 48). However these have all been done at a relatively high source-mount superficial density.

Previous observations of phenomena interpreted as due to back-scattering from a source mount in a 4π-counter have been reported (16, 25, 31). These were large compared with the corresponding effects in $\ll 2\pi$ geometries. The reason for this was attributed by Mann and Seliger (28) to a large contribution in the 4π geometry due to small-angle single-scattering.

"Coincidences in a 4π-counter" may be defined as events where both halves of the counter are discharged within the resolving time of the apparatus by a *single* disintegration. This is, of course, an entirely different phenomenon from that by which resolution losses occur at high counting rates, because the counter is unable to differentiate between *two successive* disintegrations. The "coincidences" obviously do not result in any error in the disintegration-rate determination.

This phenomenon was previously observed by Haxel and Houtermans (24), who ascribed it to conversion electrons emitted simultaneously with the β radiation of Rb^{87}. A fairly comprehensive study by Suzor and Charpak (13, 14, 46, 47, 48) pointed out three possible causes for these coincidences:

(i) Secondary electronic radiation resulting from interaction of the primary beta radiation with the source mount.

(ii) Electrons from the source, in addition to the β particle.

(iii) Very soft gamma radiation from the source.

Smith (44) interpreted his data for S^{35} on the basis of (ii) and (iii). However, Meyer-Schützmeister and Vincent (31) came to the conclusion that, in the case of S^{35} at least, the main cause was back-scattering of radiation by the counter gas and counter walls from one half-counter to the other. They considered that $<0.1\%$ of the effect observed could be attributed to inner bremsstrahlung electrons in the cases of S^{35} and P^{32}. This latter observation agrees with recent experimental work (8, 40) where inner bremsstrahlung electron emission was found to occur very much less frequently than reported by Bruner (11).

The first problem attempted in this paper is the identification of the phenomena leading to coincident discharges. Back-scattering and absorption curves, as observed in a 4π steradian counter geometry, are then obtained.

EXPERIMENTAL AND RESULTS

The counter and most of the associated equipment were the same as described earlier (38). The total counting rate N_T (with the two half-counter anodes connected in parallel) is related to the counting rates above (n_a) and below (n_b) the source mount and to the coincidence rate (n_c) by the relationship

$$N_T = n_a + n_b - n_c. \qquad [1]$$

n_c may be obtained by measuring N_T, and then n_a and n_b separately by disconnecting each anode in turn. n_c is then obtained by subtraction of two large quantities, which gives rise to a large statistical error. Alternatively, as in this work, one may use an electronic coincidence circuit which obtains the result directly.

The two counter anodes were connected to different high voltage supplies. The outputs were fed separately into Atomic Instrument Co. Ltd. 205-B Pre-Amplifiers, Atomic Energy of Canada AEP 1448 non-overloading amplifiers, and Marconi AEP 908 scalers. The output signals of the two amplifiers, taken after discrimination from the output of the multivibrator stage, were fed into an Atomic Energy of Canada AEP 1509 coincidence unit and thence to a third AEP 908 scaler. A block diagram of the equipment appears in Fig. 1.

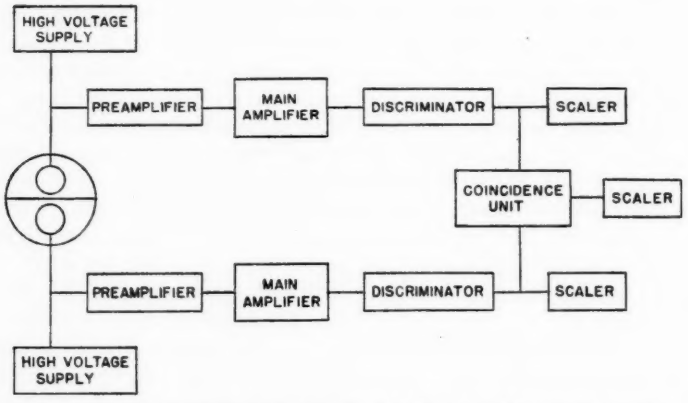

FIG. 1. Block diagram of electronic apparatus for coincidence experiments.

The two systems were shown to be matched using the threshold of the Ni^{63} plateau as a criterion.

The coincidence rates as measured were corrected for random coincidences. The rate at which random coincidences are recorded (N) when unrelated

sources of pulses occurring at rates of n_1 and n_2 are connected to the two inputs of the coincidence circuit is given by

$$N = n_1 n_2 t \qquad [2]$$

where t is the effective resolution time of the circuit. The latter was determined to be 10.3 μsec. for a range of values for n_1 and n_2 (supplied by two independent proportional counters) and this value substituted into equation [2] was used to correct all subsequent data for random effects.

A disadvantage of measuring the coincidence rate directly, involving as it does an electrical separation of the two anode systems, is the appearance of positive pulses at the amplifier output, in addition to the usual negative pulses from the electron cascade. The amplitude of these positive pulses is observed to be a function of the diameter of aperture in the diaphragm separating the two half-counters, and of the polarization potential applied to the half-counter opposite to that in which they are produced. They are found to be in coincidence with negative pulses in the other half-counter, and to be nearly independent of the state of polarization of the hemisphere in which they are observed.

All the foregoing is consistent with this effect being due to induction of a positive pulse in one anode by the movement of the electron cascade away from it, towards the other. In normal counter operation, connection of the anodes in parallel eliminates the effect since the small positive pulse merely slightly reduces the amplitude of the negative pulse normally measured. In the coincidence experiments, the positive pulses are amplified but fail to trigger the discriminator circuit and so do not register. However, above 2.6 kv. polarization potential, the negative overshoot following the larger positive pulses begins to be effective in triggering the discriminator, and with the relatively long resolving time in use (10.3 μsec.), spurious coincidence counts are produced. In the experiments to be described below, conditions were always such that these spurious coincidences did not occur. The presence of these induced pulses of opposite sign, however, should always be considered in experiments where two halves of a 4π-counter are used separately.

The experimental results to be presented here fall into two main categories:

(*a*) The coincidence rate n_c was determined as a function of various diaphragm aperture sizes at a suitable polarization potential using β emitters with maximum energies covering the range 67 to 1700 kev. Methane, and argon +10% methane were the two counter filling gases used. In all cases but that of Ni^{63}, the sources were point sources prepared by evaporation of a carrier-free solution. For Ni^{63} the source was prepared as nickel dimethylglyoxime by a vacuum distillation method to be described in a forthcoming publication. Each source was prepared on a gold-coated VYNS film (5–10 μgm./cm.^{2}) which had been mounted over 5 cm. aperture. Measurements of n_a, n_b, n_c were made and N_T computed. A diaphragm with a smaller aperture was then placed over the film, and the measurements were repeated for a series of aperture sizes in this manner. The results of this series are plotted in Figs. 2 and 3. N_T was found to be independent of aperture size.

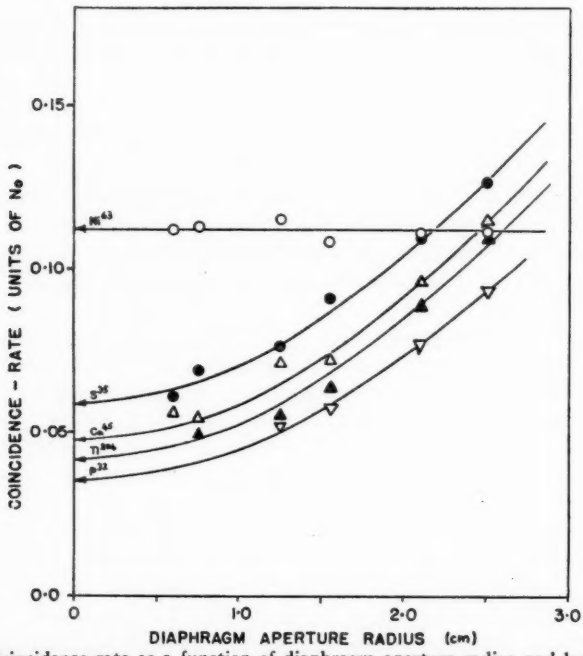

FIG. 2. Coincidence rate as a function of diaphragm aperture radius and beta end-point energy for methane counting gas.

(*b*) n_c, n_a, and n_b were measured for the same series of nuclides plus the α emitter Po^{210} as a function of source-mounting film-thickness with each of the counting gases mentioned. The aperture diameter remained constant at 2.5 cm. The sources were identical to those described previously. The results are shown in Fig. 4. In addition a thick source of Ni^{63} (2.6 mgm./cm.) was prepared. These curves show no features differing from those observed with the thin source, other than the expected additional absorption.

In all experiments at least 1000 coincidence events were recorded, giving a standard deviation of $\pm 3\%$.

In order to check on the operation of the counter with the greater mount thicknesses, the Ni^{63} characteristic was periodically checked. This at no time showed any unexpected features.

DISCUSSION

(*a*) *The Coincident Discharges*

The frequency of occurrence of the coincident discharges (as high as 20% of the disintegration-rate of pure β emitters even with very thin source mounts) allows one to eliminate many of the possible causes of this phenomenon. A low production probability, coupled in the relevant cases with a low counter response to photons, is sufficient to eliminate nuclear gamma radiation,

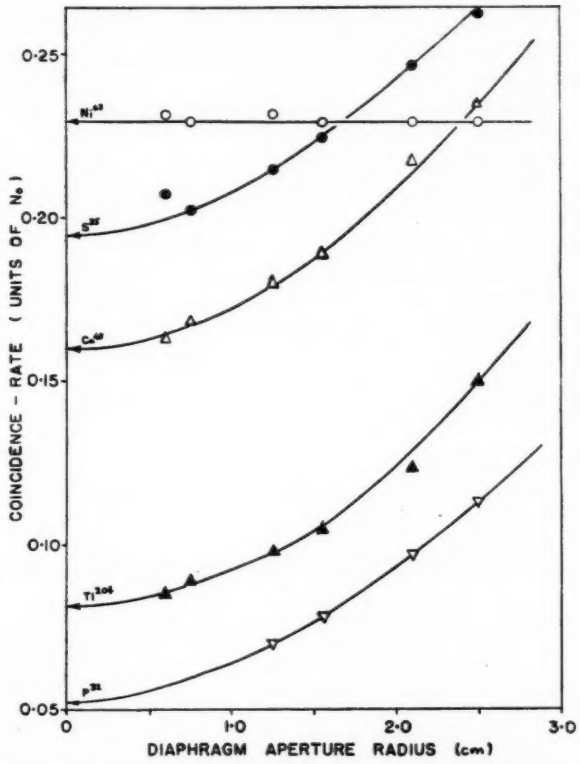

FIG. 3. Coincidence rate as a function of diaphragm aperture radius and beta end-point energy for argon + 10% methane counting gas.

conversion electrons, inner bremsstrahlung, and inner bremsstrahlung electrons (7, 9, 10, 35, 43, 49). Similarly bremsstrahlung production (3, 49) and secondary electron production (32, 33, 36) in the very thin film can be shown to be several orders of magnitude too low. Corresponding processes in the counter gas and walls may also be ruled out owing to absorption in the source-mount diaphragm and unfavorable geometrical conditions.

It appears that the only process of sufficient magnitude which could be responsible for a significant proportion of the coincidence events is back-scattering of radiation by the counter gas and counter walls into the other half-counter. (Back-scattering effects with $\ll 2\pi$ counters, e.g. end-window counters, have been shown to be of the necessary order of magnitude.) The rate of occurrence of coincidences due to scattering close to the source will be independent of the aperture diameter. That due to scattering further away from the source will increase with aperture diameter while that due to scattering at large distances will be proportional to the square of the aperture diameter.

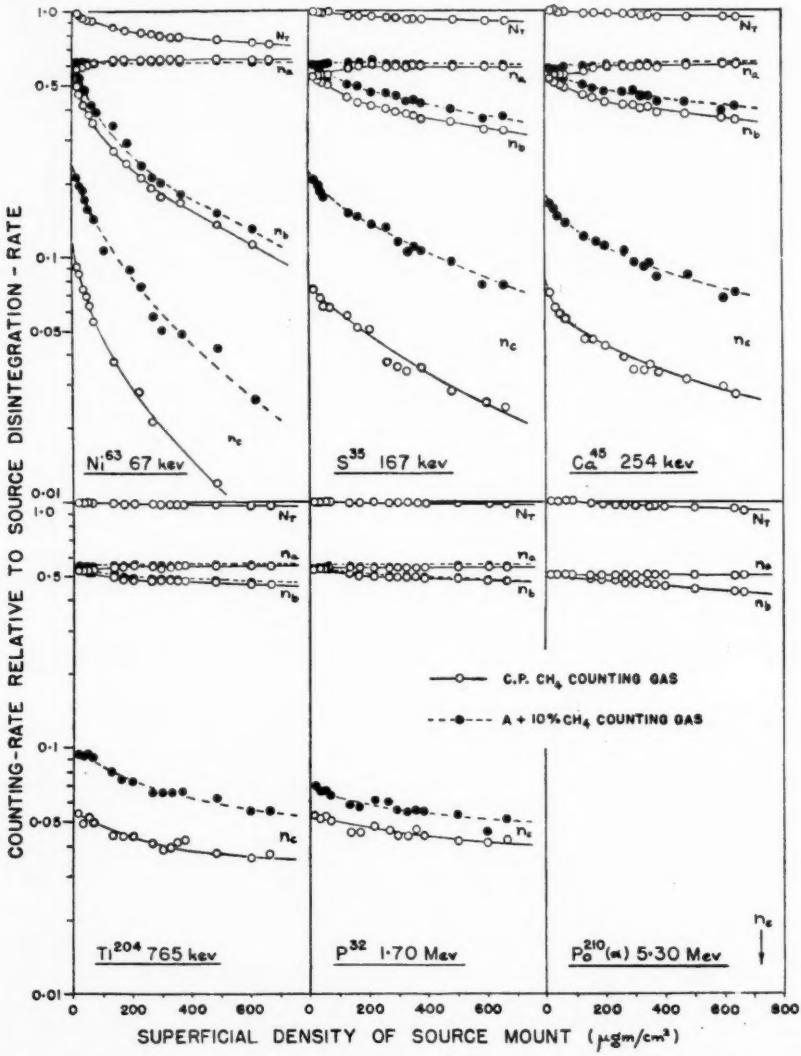
COUNTING-RATE RELATIVE TO SOURCE DISINTEGRATION - RATE
SUPERFICIAL DENSITY OF SOURCE MOUNT (μgm/cm²)
Ni⁶³ 67 kev
S³⁵ 167 kev
Ca⁴⁵ 254 kev
Tl²⁰⁴ 765 kev
P³² 1·70 Mev
Po²¹⁰(α) 5·30 Mev
C.P. CH₄ COUNTING GAS
A + 10% CH₄ COUNTING GAS

FIG. 4. Total counter, half-counter, and coincidence counting rates as a function of source-mount superficial density for beta emitters of increasing end-point energy and for Po^{210} alpha radiation for methane and argon+10% methane counting gases.

The contribution from either or both of these processes may be obtained from the data in Figs. 2 and 3. If the curves are extrapolated to $r = 0$, that part of the coincidence phenomenon which is independent of r can be separated. In Fig. 5 the values of n_c at $r = 0$ are plotted against the maximum energy of the β emitter. The values obtained for each counter gas lie on a smooth

curve and can be attributed to back-scattering from the gas in the neighborhood of the source. The relative positions of the curves for argon–methane ($\bar{Z} = 16$) and methane ($\bar{Z} = 2$) are consistent with the increased scattering expected (4) and observed by Yaffe and Justus (50) using material of higher atomic number. The form of the curves obtained here is similar to that observed by these authors for back-scattering from a constant thickness back-scatterer as a function of particle energy, if one neglects the fall-off they observed at very low energies. (This fall-off is undoubtedly due to preferential absorption of the back-scattered radiation in the counter window.)

The value of n_e for Ni^{63} is independent of aperture size as shown in Figs. 2 and 3. This is to be expected owing to the soft nature of this β radiation. An appreciable scattering will occur close to the source. Any other radiation will be absorbed by the counter gas.

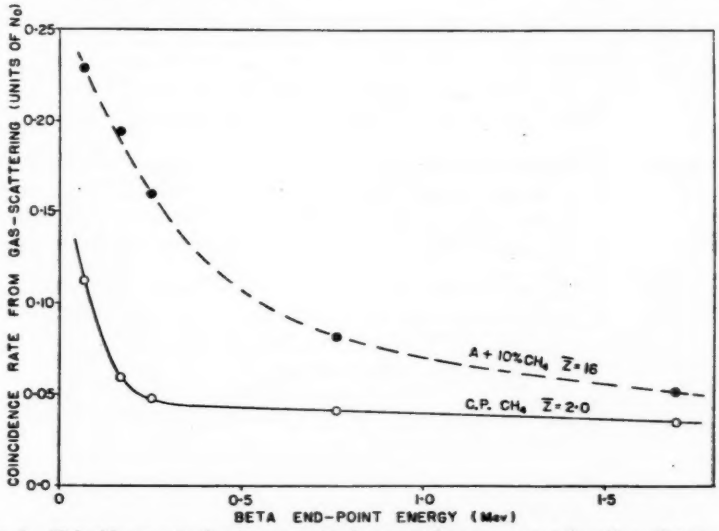

FIG. 5. Coincidence rate due to gas-scattering near the source, as a function of beta end-point energy for methane and argon+10% methane counting gases.

Measurements of Po^{210} α particles, as shown in Fig. 4, give values for n_e of less than 0.1% of the disintegration rate. This agrees with the foregoing interpretation since α radiation, for which the diffusion mechanism does not occur, can only back-scatter by large-angle single or plural scattering events, which are highly improbable. This value of 0.1% also serves as an upper limit enabling one to confirm that many of the processes suggested by other workers, e.g. secondary electron production by interaction with the source mount, are unimportant in this case.

Our conclusions regarding the origin of the coincidence phenomena agree with those of Hawkings (23), who studied the variation of coincidence rate with counting gas pressure using a S^{35} source.

(*b*) *Absorption and Scattering of β Radiation by the Source-mounting Film*

The curves shown in Fig. 4 can be resolved into the appropriate absorption and scattering components using methods somewhat similar to those used previously in calculations of this type (28, 44). Our treatment will however consider these components as functions of β particle energy and film thickness. One can assume a response probability of the counter of unity towards electrons and can neglect all processes involving the production of secondary electronic radiation as before. The relevant processes are absorption and elastic scattering in the source-mount film and back-scattering of electrons by the electron diffusion process near and far from the source.

During this part of the experiment the aperture diameter of the diaphragm between the two half-counters remained constant at 2.5 cm. If E is the maximum energy of the β radiation and d the film thickness, one can let

$p_1(E, d)$ = transmission of the film to the incident β radiation from the source,

$p_2(E, d)$ = the probability that β radiation originally emitted into the 2π steradian solid angle towards hemisphere A will be scattered by the film so as to enter the other hemisphere B,

$p_3(E)$ = the probability that the β radiation incident into either hemisphere is back-scattered by the counter gas at a distance small compared to the aperture diameter so as to enter the other hemisphere (one can neglect the small energy degradation by the film),

$p_4(E)$ = the probability that the β radiation incident into either hemisphere is back-scattered by the counter gas and/or counter walls at a distance comparable to or greater than the aperture diameter so as to enter the other hemisphere,

$p_5(E, d)$ = the transmission of the film to the back-scattered radiation arising from processes 3 and 4.

Other second-order effects may justifiably be neglected, e.g. wall scattering of back-scattered particles.

Using the above probabilities, the following expressions for the half-counter and coincidence counter rates are obtained where N_0 is the disintegration rate of the sample.

[3] $$n_a = \tfrac{1}{2}N_0[(1+p_2) + p_1 p_3 p_5 + p_1 p_4 p_5]$$

(incident + film scattering; near gas back-scattering from other hemisphere; far gas and wall back-scattering from other hemisphere)

[4] $$n_b = \tfrac{1}{2}N_0[(1-p_2)p_1+p_3 p_5+p_4 p_5]$$

[5] $$n_c = \tfrac{1}{2}N_0[p_3 p_5+p_1 p_3 p_5+p_1 p_4 p_5+p_4 p_5].$$

At $d = 0$, $p_5 = p_1 = 1$, and $p_2 = 0$,

$$n_{a_0} = n_{b_0} = \tfrac{1}{2}N_0[1+p_3+p_4],$$

and $$n_{c_0} = N_0[p_3+p_4].$$

Also $$N_T = n_a+n_b-n_c = \tfrac{1}{2}N_0[1+p_2+(1-p_2)p_1],$$

and at $d = 0$ $$N_T = N_0.$$

This agrees with the expectation that N_T will be independent of the factors governing the magnitude of the coincidence rate and differs from N_0 only owing to absorption in the film of that part of the radiation which escapes back-scattering. The values of n_a, n_b, and n_c can be obtained from Fig. 4. p_3 and p_4 are taken from Figs. 5 and 2 respectively. The unknown quantities p_1, p_2, and p_5 are obtained by substituting a series of values of E and d in equations [3], [4], and [5], and solving them simultaneously. The results are shown in Figs. 6 and 7.

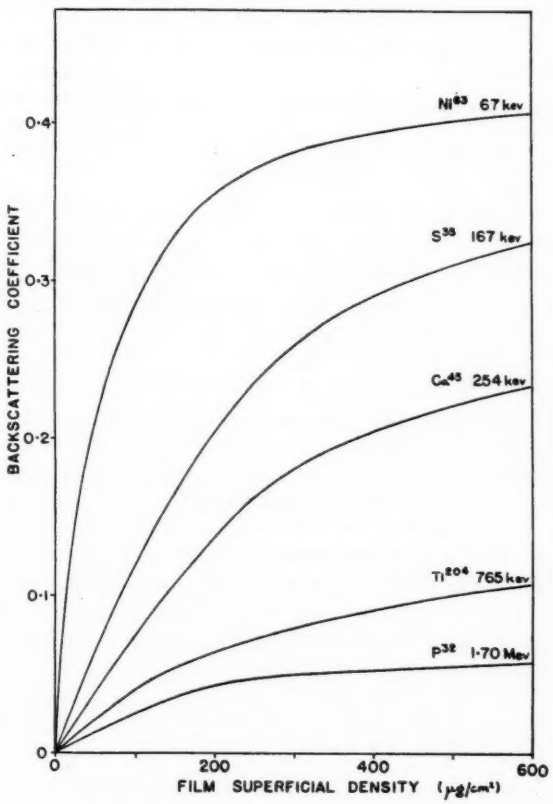

FIG. 6. Source-mount back-scattering coefficient (p_2) as a function of film superficial density for beta emitters of increasing end-point energy.

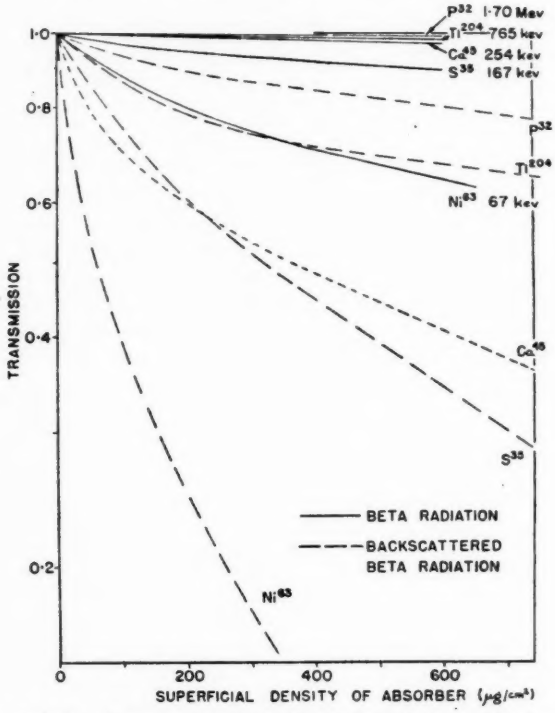

FIG. 7. Transmission of source mount to incident beta radiation (p_1) and to back-scattered beta radiation (p_2) as a function of film superficial density for beta emitters of increasing end-point energy.

Back-scattering of β Radiation from Thin Films

The curves of p_2, the film back-scattering coefficient, bear a superficial resemblance to the results of previous work using $\ll 2\pi$ counter systems. The magnitude of the effect observed here is much larger at low film thicknesses in agreement with the previous observations by other workers (14, 47, 48), who used much thicker films than we did. In contradistinction to the $< 2\pi$ systems, back-scattering at a given mount thickness was found to be greatest for the lowest energy β emitter. This is consistent with the suggestion that the scattering effects observed here are due to single scattering events involving electrons incident at small angles to the film, rather than to the electron diffusion type of back-scattering. The Rutherford-type scattering of relativistic electrons by atoms, described for example by McKinley and Feshbach (30), will occur predominantly at very small angles, will fall off rapidly as the scattering angle increases, and will be greatest for small electron energies.

Absorption of Incident and Back-scattered Radiation

In Fig. 7 the absorption curves for the incident and the back-scattered β radiation are compared. The energy degradation of the back-scattered radi-

ation is found to be much greater than that observed in the $\ll 2\pi$ system. In the latter case a ratio of 0.4–0.8 for the ratio of half-thicknesses or ranges of the back-scattered to the incident radiation is found. In this work, for Ni^{63} for example, we find a half-thickness ratio of about 0.05. Our results, in agreement with those of Balfour (1), clearly indicate the existence of a large proportion of very low energy particles in the spectrum of the back-scattered radiation. This is observable because of the "windowless" nature of the counter.

(*c*) *"Sandwich" Procedure for Correcting for Source-mount Absorption Losses*

It was shown in an earlier publication (39) that the correction for source-mount absorption losses by the "sandwich" method leads to erroneous values being obtained for the source disintegration rate. Mann and Seliger (28) formulated the following expression for the fractional absorption τ in a film,

$$\frac{\tau}{2} = \frac{N_T - N_S}{2N_T - N_S},$$

where N_T and N_S are the counting rates observed for a source mounted on one film and in a "sandwich" respectively.

By inspection, using nomenclature as defined above, $N_S = N_0 . p_1$ and

$$\frac{\tau}{2} = \frac{(1-p_1)(1+p_2)}{2(1+p_2-p_1p_2)}.$$

If one assumes as Mann and Seliger have done that p_2, the back-scattering by the film, is negligible, then τ would equal $(1-p_1)$, the film absorption as expressed in our nomenclature. However one can see from Fig. 6 that p_2 cannot be neglected without introducing a fairly large error. Mann and Seliger assumed also that

$$N_T = N_0 - \tfrac{1}{2} N_0 . \tau,$$

i.e. that half the emitted radiation entered the film and a fraction of this would be absorbed. However this half is reduced by the back-scattered portion. This introduces an error in the opposite direction. Despite this fortuitous cancellation of errors, the "sandwich" process can only be considered as an approximation in disintegration-rate determinations.

ACKNOWLEDGMENTS

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A DIELECTRIC STUDY OF PLASTICIZED POLYVINYLIDENE CHLORIDE[1]

By B. L. Funt and T. H. Sutherland[2]

ABSTRACT

The electrical response of plasticized polyvinylidene chloride has been studied over a wide range of frequency, temperature, and plasticizer content. The dispersion region was shifted to lower temperatures at a given frequency on the addition of alpha chloronaphthalene as plasticizer, but remained practically unchanged with hexachlorobenzene as plasticizer. Comparison was made with mechanical measurements for plasticized vinylidene chloride copolymers and reasonable agreement between electrical and mechanical properties was found. Enthalpies and entropies for dielectric relaxation were calculated on the theory of absolute reaction rates and were compared with values for plasticized polyvinyl chloride. A calculation of plasticizer efficiency from electrical measurements was attempted on the basis of a method suggested by Dyson. An interesting empirical relationship between enthalpy and entropy of activation and plasticizer content in polyvinyl chloride and polyvinylidene chloride is presented.

Previous studies of the electrical response of plasticized polymers have contributed to the elucidation of the mechanism of interaction between a polar polymer and a plasticizer. In general the presence of a plasticizer serves to decrease the attractive forces between neighboring polymer chains and results in a softer and more pliable material. In a polar polymer, this increased freedom of molecular movement will be evident in a corresponding increase in the ability of polar groups to respond to an applied alternating electric field. The ease with which dipoles follow the impressed field can be measured by the characteristic Debye dispersion curves at a given temperature. Where a strong intermolecular attraction exists dielectric dispersion will occur at a relatively low frequency at which a sigmoidal change of dielectric constant with frequency and the appearance of a loss factor maximum will be exhibited. On the addition of plasticizer the dispersion region shifts to higher frequencies indicating a lower internal viscosity and a greater freedom of chain movement.

While the general features of plasticizer action and their investigation by dielectric methods were established by Fuoss (7, 8, 9, 10, 11, 12, 13, 14, 17) there has been considerable latitude in the quantitative interpretation of the data. Attempts have been made to relate plasticizer efficiency to size, shape, and polarity of the plasticizer molecule and to correlate electrical and mechanical properties (19). Although a relatively large number of investigations have been reported almost all of them have been confined to the study of plasticized polyvinyl chloride (2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 17). Consequently the validity and generality of many of the theoretical comparisons have rested on the experimental confirmation found with this polymer.

It therefore appeared advisable to initiate experimental work with other similar polar plasticized polymers in order to test some of the current views

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of the dielectric interpretation of plasticizer action. Vinylidene chloride was selected for its chemical similarity to vinyl chloride.

APPARATUS

The electrical apparatus has been described previously (6, 18). In the current work a General Radio precision sample holder was used. The side plates were removed from the holder in order to permit its being thermostatted in an air thermostat maintained to ±0.05°C. A thermocouple was inserted in the housing of the sample holder to provide a further check of the sample temperature.

CHEMICALS

Polyvinylidene chloride (Saran A) of weight average molecular weight 10,000 and 100,000 was provided through the courtesy of the Dow Chemical Company.

Alpha chloronaphthalene, Eastman, reagent grade, was used as obtained. The lead stearate used was Wittco No. 10, and was not purified further.

The samples were prepared by treating the pulverized polymer in a 70:30 mixture of benzene and 2-butanone to which the plasticizer was added. After refluxing for four to five hours the samples were dried *in vacuo* for 24 hr. and then pressed into thin disks at a temperature of 135–165°C. and a pressure of 5000 lb./in^2.

After cooling, the samples were coated with aquadag and then placed into the sample holder.

RESULTS

The dielectric constant and loss factor of each sample was measured at frequencies of 50, 100, 300, 1000, 3000, 10,000, 30,000, and 100,000 cycles per second at temperature intervals of 5°C. throughout the dispersion range. The data are shown graphically in Figs. 1 to 6 for concentrations of 0 to 24.8% alpha chloronaphthalene plasticizer by weight.

The addition of a good plasticizer progressively decreases the temperature at which dispersion occurs at a given frequency. For instance, the maximum of the loss factor curve (f_{max}) changes by 35°C. from the unplasticized to the most plasticized sample at 3 kc. A plot of log f_{max} versus reciprocal temperature is expected to yield a straight line whose slope determines ΔH^*, the free enthalpy of activation. Such plots are shown in Fig. 7 for the data obtained at 3 kc. with alpha chloronaphthalene. Pronounced curvature is shown, particularly if the 100 kc. points are included. For the data in Table I the slopes were determined by the method of least squares, and weighting factors were used to compensate for the lower precision at the extremes of frequency. The relative weighting factors at each frequency were 50 c.p.s. (3), 100 c.p.s. (3), 300 c.p.s. (4), 1 kc. (4), 3 kc. (4), 10 kc. (4), 30 kc. (3), and 100 kc. (1). The curvature shown in the plots for activation energy is not new; a similar phenomenon is shown in Dyson's data for polyvinyl chloride (3).

The free energies, enthalpies, and entropies for dielectric relaxation were calculated by the method described by Kauzmann (16) and are also tabulated in Table I.

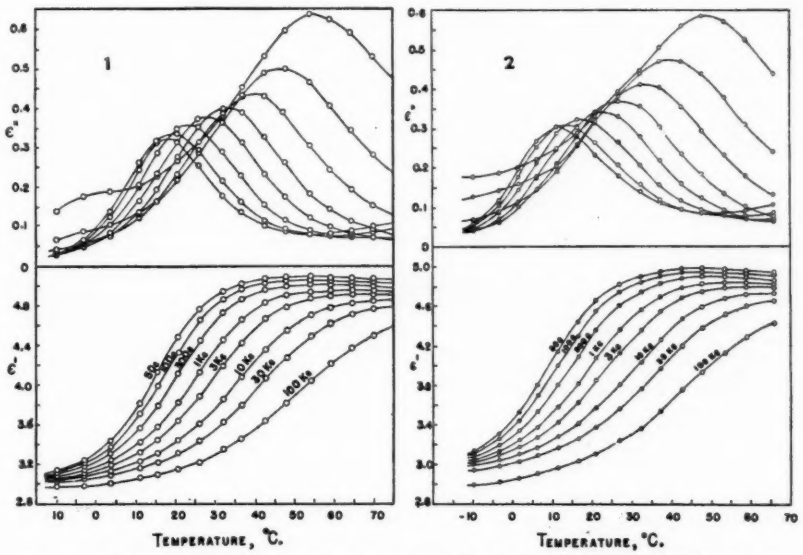

FIG. 1. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 stabilized with 1% by weight of lead stearate.

FIG. 2. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 containing 3.1% by weight alpha chloronaphthalene and 1% lead stearate.

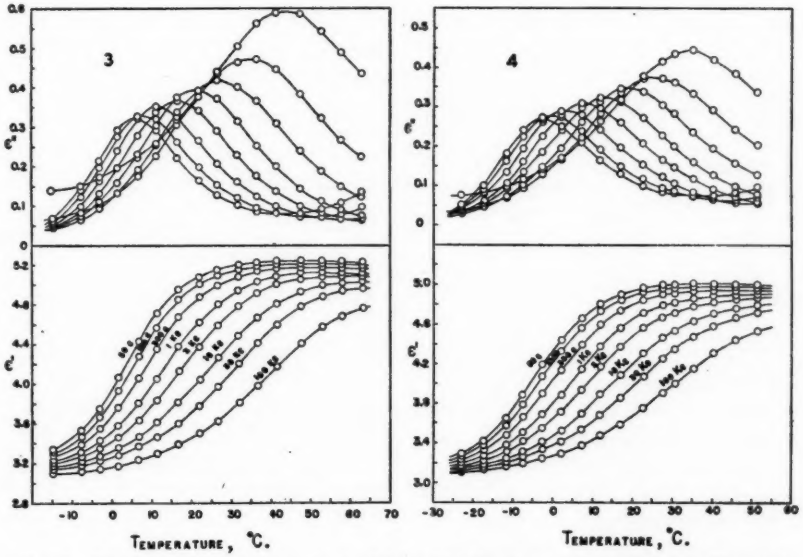

FIG. 3. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 containing 6.0% by weight alpha chloronaphthalene and 1% lead stearate.

FIG. 4. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 containing 10.1% by weight alpha chloronaphthalene and 1% lead stearate.

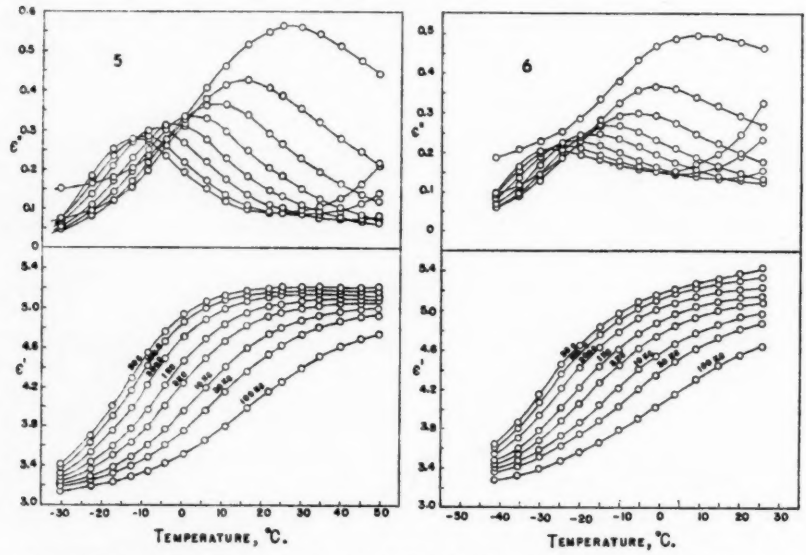

FIG. 5. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 containing 15.1% by weight alpha chloronaphthalene and 1% lead stearate.

FIG. 6. Dielectric dispersion in polyvinylidene chloride of molecular weight 10,000 containing 24.8% by weight alpha chloronaphthalene and 1% lead stearate.

TABLE I

ENTHALPIES ΔH^*, ENTROPIES ΔS^*, AND CHARACTERISTIC TEMPERATURES (T_s) FOR SYSTEMS INVESTIGATED, AS FUNCTIONS OF POLYMER AND PLASTICIZER CONCENTRATION

Sample	ΔH^* (kcal.)	ΔS^* (e. u.)	Mole fraction polymer	Weight % polymer	Density (gm./cc.)	T_s (°C.)
Hexachlorobenzene						
B	42.55	100.2	99.5	98.0	1.741	268.1
B1	39.53	91.8	98.2	94.6	1.736	263.0
B2	41.29	96.6	96.9	91.1	1.762	266.2
B3	40.56	94.1	95.2	86.7	1.781	265.8
B4	41.20	96.5	92.0	79.2	1.812	265.7
B5	40.46	93.8	89.6	74.3	1.804	265.5
B6	40.97	96.3	74.4	49.5	1.886	264.6
B7	41.41	96.7	46.2	24.8	1.933	266.7
Alpha chloronaphthalene						
C1	39.56	92.2	97.6	95.9	1.752	262.5
C2	37.76	88.7	95.8	93.0	1.702	256.5
C3	36.12	86.9	93.3	89.0	1.697	248.5
C4	34.21	84.5	89.9	84.0	1.678	239.5
C5	29.94	76.0	82.8	73.9	1.635	223.1
Unplasticized polymers						
P	40.08	91.2	99.5	99.0	1.751	267.6
S-1	40.75	90.0	100.0	100	1.736	272.6
S-2	41.93	93.7	100.0	100	1.732	275.3
T	38.45	83.9	100.0	100	1.290	269.8

The data of Table I can be compared with similar data obtained from dielectric investigations of other polymer systems, and for plasticized polyvinyl chloride. For a given comparison the relative magnitudes of the enthalpies and entropies of activation are significant, and reflect freedom of movement of segments of the polymer chains.

It can be seen from Table I that for alpha chloronaphthalene, which is a relatively good plasticizer for polyvinylidene chloride, the dispersion region is shifted to lower temperatures with increasing plasticizer content. The enthalpy and entropy values are also lowered corresponding to increased freedom of segmental motion in the polymer chains. With hexachlorobenzene, however, the effect of plasticizer is very slight, the temperature range of the dispersion region remains unchanged, and the enthalpy and entropy values remain relatively constant even at plasticizer concentrations of 75% by weight. One must conclude that true plasticization is not occurring in this instance, and that a macro dispersion of plasticizer in polymer is being obtained.

The results with different unplasticized polymers are also shown in Table I. Polymer S-1 was a Dow Chemical Co. sample of weight average molecular weight 10,000 and S-2 was a similar sample of molecular weight 100,000. Sample P was obtained from S-1 on the addition of 1% by weight of lead stearate as a thermal stabilizer. Sample T was obtained by emulsion polymerization of vinylidene chloride under nitrogen at 25°C. using a persulphate activator, and was not fractionated.

The results obtained with these materials confirm the slight dependence of the position of the dispersion region on molecular weight. This is doubtless due to the segmental nature of the electrical response (16).

The mechanical properties of a vinylidene chloride 85% – vinyl chloride 15% copolymer have been reported by Havens (15). These data can be compared with the electrical results obtained in the present work. For this purpose we define temperature T_x obtained by extrapolation of the electrical data to a relaxation time τ of one second, where the relaxation time is defined as 2π times frequency of maximum absorption. The relaxation time of one second is comparable to that of a mechanical test, and is usually chosen where a comparison of electrical and mechanical properties is desired.

In Fig. 7 the flex temperatures determined by Havens and T_x values obtained in this work are plotted against plasticizer content for comparison. It is evident that quite good agreement is obtained.

A most detailed interpretation of data on plasticized polymers has been attempted by Dyson (3). If a typical relaxation mechanism involves n monomer units, then the enthalpy of activation, ΔH^*, is nM calories per mole where M is the attractive energy between two chains per monomer length. For vinylidene chloride M has been reported as 1890 cal. per unit (1). If there are r alternative configurations available in the excited state the n monomer units will have r^n configurations available and the entropy of activation can be expressed as

$$S^* = R \ln r^n$$

where R is the gas law constant.

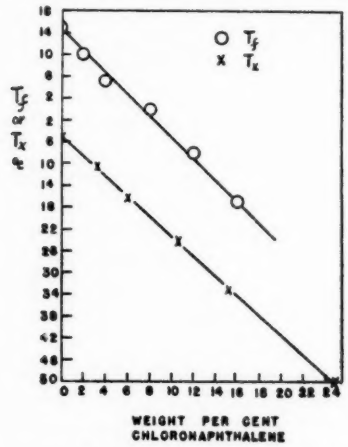

FIG. 7. Comparison of mechanical and electrical data.

Dyson has further elaborated his argument to include plasticized systems. He suggests that a plot of $1/\Delta H^*$ against volume fraction plasticizer should yield a straight line whose slope could be interpreted to indicate the tendency for plasticizer molecules to 'cluster'. The present data (and some of the data on polyvinyl chloride) do not yield a good linear relationship. Nevertheless the slope of the best line was taken and using the appropriate data a value for q of 6 was obtained for alpha chloronaphthalene, and a value approaching infinity for hexachlorobenzene. The significance of q on this picture is that it represents the number of plasticizer molecules in a cluster. One would interpret a large value of q as indicative of poor plasticizer action and a low value as giving high plasticizer efficiency. Corresponding values for polyvinyl chloride are 4.4 and 2.3 with tricresyl phosphate, 4.8 with diphenyl, and 1.7 with dioctyl phthalate, according to Dyson. These latter values would be reduced by the factor 1040/1520 if Bunn's recent values for cohesive energy (1) are used instead of those adopted by Dyson.

An interesting empirical relationship between plasticizer content and enthalpy and entropy of activation was discovered. It was found that on a logarithmic plot of enthalpy of activation against mole per cent polymer the data for all good plasticizers for a given polymer were found to fall on the same straight line. This is shown in Fig. 8 where the data of Fuoss for tetralin and diphenyl and of Daniels, Miller, and Busse for tricresyl phosphate as recalculated by Dyson (3), and of Fitzgerald and Miller (5) for dimethyl thianthrene plasticizers in polyvinyl chloride are shown. It should be noted that Dyson's treatment of enthalpy data yields different slopes for different plasticizers. The present empirical relationship shows agreement for all good plasticizers in a given polymer. Our data for polyvinylidene chloride plasticized with alpha chloronaphthalene are shown in Fig. 9. Again the agreement with a

linear relationship is reasonable, but the slope of the line is different for this polymer than for polyvinyl chloride.

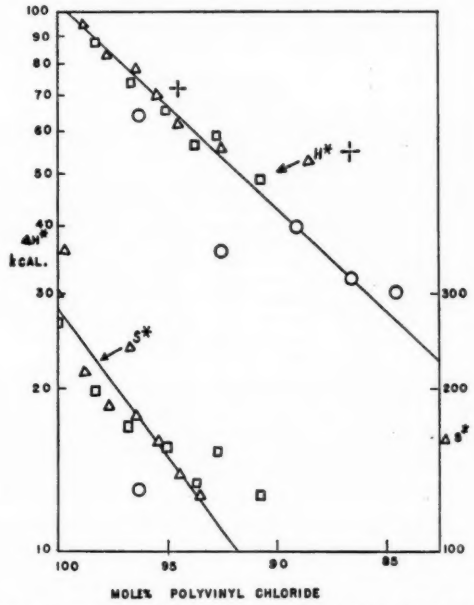

FIG. 8. Enthalpy and entropy of plasticized polyvinyl chloride as a function of polymer content. Plasticizer: tetralin (O), diphenyl (Δ), tricresyl phosphate (□), dimethyl thianthrene (+).

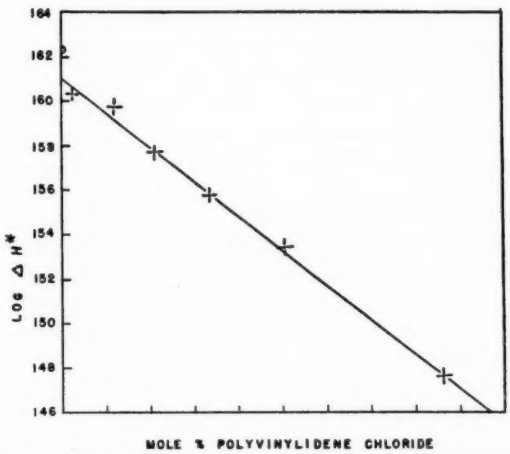

FIG. 9. Enthalpy of polyvinylidene chloride plasticized with alpha chloronaphthalene as a function of mole per cent polymer.

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SOME CALCULATIONS OF THE SURFACE ENERGY OF MAGNESIUM OXIDE[1]

By G. C. Benson and R. McIntosh[2]

ABSTRACT

Calculations of the surface energy of an undistorted {100} face of crystalline magnesium oxide have been made. An exponential form of the repulsive energy term was used, and the van der Waals attractive energy between dipoles was included, as in the Born–Mayer treatment of cohesive energy. Comparison with earlier work is made, and it is shown that results are markedly dependent upon the form of the repulsive potential term, the inclusion of the van der Waals term, and, indeed, the choice of coefficients of the van der Waals term. This is not the case so far as the calculated cohesive energies are concerned. The results indicate that a Born–Mayer model may be inadequate in the case of magnesium oxide, and that caution must be exercised before accepting surface energies arrived at by such calculations.

INTRODUCTION

In early theoretical calculations concerning the properties of ionic crystals the potential energy of interaction between ions was taken to be the sum of the coulombic and the repulsive terms. Originally the latter was represented through an inverse power law, but this was later replaced by an exponential form more in accord with a quantum mechanical consideration of the interaction between closed shells of electrons. A further refinement was the inclusion of terms for the van der Waals attraction between the ions. This model of an ionic crystal, usually referred to as the Born–Mayer model, has been quite successful in explaining the cohesive properties of the alkali halides and other ionic crystals. It has also been adopted in calculations of the surface energy of such crystals. In this case the theoretical problem is complicated by the asymmetrical field at the surface, which leads to polarization of the ions and distortion of the lattice near the surface. Consideration of these effects by Lennard-Jones and Dent (12) and Verwey (21) indicates that they will lead to a decrease of the surface energy below the value calculated for an undistorted crystal. Calculations due to Shuttleworth (18) show that although the van der Waals terms play a rather minor role in the cohesive energy of the alkali halides, they make a substantial contribution to the calculated surface energy of these crystals.

Unfortunately there are very few experimental data on which to base a judgment of the utility of the Born–Mayer theory in calculating surface energies. In the case of sodium chloride (3) the experimental evidence, though admittedly inconclusive, is that the surface energy is higher by a factor of two or three than the value obtained by the application of the Born–Mayer theory. The only other material for which data are available is magnesium oxide, for which Jura and Garland (10) have reported a surface energy of 1040 ergs per cm.^{2}, in good agreement with the only available theoretical value calculated

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by Lennard-Jones and Taylor (13) some thirty years ago. Since in their calculation Lennard-Jones and Taylor employed the older form of repulsive potential (an inverse 10th power) and did not consider the van der Waals contribution, a reinvestigation of the problem is of some interest and is the purpose of the present communication.

METHOD OF COMPUTATION

According to the Born–Mayer (4) theory, the cohesive energy at 0°K. of a bivalent ionic crystal of sodium chloride type structure is given by

$$U = 1.7476 \times \frac{4\epsilon^2}{r_0} + \left[a_{+-}A_6' + \left(\frac{a_{++}+a_{--}}{2}\right)A_6''\right]\frac{1}{r_0^6} - 6b[(e^{(r_++r_-)/\rho})\, e^{-r_0/\rho} + (1.5\, e^{2r_+/\rho} + 0.5\, e^{2r_-/\rho})\, e^{-\sqrt{2}\, r_0/\rho}].$$

In this equation zero point energy and van der Waals terms higher than those between dipoles have been omitted. The symbols employed are defined as follows:

r_0 is the nearest neighbor distance at 0°K.,
ϵ is the value of the electronic charge,
a_{++}, a_{--}, a_{+-} are van der Waals coefficients,
A_6', A_6'' are lattice sums tabulated by Jones and Ingham (9),
r_+, r_- are the Pauling radii of the ions,
b, ρ are the constants in the expression for the repulsive potential.

The corresponding expression for the surface energy of an undistorted {100} face of the crystal, that is, neglecting polarization of ions and changes of lattice spacing, is

$$\sigma = \frac{1}{2r_0^2}\left\{0.065246 \times \frac{4\epsilon^2}{r_0} + \left[a_{+-}B_6' + \left(\frac{a_{++}+a_{--}}{2}\right)B_6''\right]\frac{1}{r_0^6} - b[(e^{(r_++r_-)/\rho})\, e^{-r_0/\rho} + 2(1.5\, e^{2r_+/\rho} + 0.5\, e^{2r_-/\rho})\, e^{-\sqrt{2}\, r_0/\rho}]\right\}$$

where B_6', B_6'' are lattice sums tabulated by Shuttleworth (18).

In applying these equations to magnesium oxide, difficulties arise in connection with the choice of the van der Waals coefficients and the constants in the term for the repulsion. Mayer and Maltbie (15) in their calculations of the cohesive energy employed $\rho = 0.345 \times 10^{-8}$ taken from previous work on the alkali halides. This choice was apparently dictated by the fact that the authors wished to deal with a series of alkaline earth oxides, and compressibility and other data necessary for a more direct adjustment of ρ were not available for the entire series. de Boer and Verwey (7) in repeating these calculations have also taken $\rho = 0.345 \times 10^{-8}$. Both groups of authors pointed out that this value of ρ is probably too small. In the present work, Bridgman's data for the compressibility and thermal expansion of magnesium oxide (5), together with a nearest neighbor spacing of 2.101$_6$ Å (22) at 30°C., have been used to calculate ρ and b in the manner outlined by Born and Mayer (4).

In treating the van der Waals term there is considerable uncertainty in the

choice of the "a" coefficients. Several possibilities have been considered, and thus this term is:

(a) Omitted.

(b) Evaluated from the London formula (14) using the ionization potential of Mg^{++} (1), the electron affinity of O^- in the crystal estimated from the edge of the ultraviolet absorption spectrum of the magnesium oxide crystal* (19), and the polarizabilities of the Mg^{++} (17) and O^{--} (20) ions.

TABLE I

COEFFICIENTS USED IN THE VAN DER WAALS INVERSE SIXTH POWER ATTRACTIVE POTENTIAL TERM

Source of coefficients	$a_{+-} \times 10^{60}$	$a_{++} \times 10^{60}$	$a_{--} \times 10^{60}$
(b) London formula and ultraviolet absorption	3.25	0.854	50.7
(c) Kirkwood–Müller formula	8.64	1.19	143
(d) Fowler	14.5	2.38	135

TABLE II

COHESIVE ENERGY OF MAGNESIUM OXIDE IN 10^{-12} ERG PER MOLECULE

Specification of model	$r_0 \times 10^8$, cm.	$\rho \times 10^8$, cm.	$b \times 10^{12}$, ergs	$\epsilon \times 10^{10}$, e.s.u.	Contributions from: Electrostatic term	Repulsive term	van der Waals term	Total omitting zero point energy
Our calculation (a) no van der Waals term	2.093	0.4427	1.871	4.8024	77.0	−14.5	—	62.5
Our calculation (b) van der Waals coefficients from London formula	2.093	0.4353	1.966	4.8024	77.0	−15.2	0.8	62.6
Our calculation (c) van der Waals coefficients from Kirkwood–Müller formula	2.093	0.4245	2.134	4.8024	77.0	−16.4	2.2	62.8
Our calculation (d) van der Waals coefficients from Fowler	2.093	0.4220	2.179	4.8024	77.0	−16.6	2.6	63.0
Lennard-Jones and Taylor r^{-11} force of repulsion	2.10	—	—	4.77	75.7	− 7.4	—	68.3
Mayer and Maltbie exponential repulsion with ρ from alkali halides and includes a van der Waals term	2.09	0.345	—	—	76.3	−11.5	0.1	64.9
de Boer and Verwey treated as in preceding entry	2.10	0.345	1.58	—	76.0	−11.2	0.1	64.9
Exponential repulsion with $\rho = 0.345 \times 10^{-8}$ and van der Waals coefficients as in (c)	2.10	0.345	1.85_2	4.77	75.7	−13.1	2.2	64.8

Suggested in a private communication from Professor Mayer.

TABLE III*

SURFACE ENERGY OF MAGNESIUM OXIDE IN ERGS PER CM.^{2}

Specification of model	Contributions from:			Total
	Electrostatic term	Repulsive term	van der Waals term	
Our calculation (*a*) no van der Waals term	3284	−3582	—	−298
Our calculation (*b*) van der Waals coefficients from London formula	3284	−3742	307	−151
Our calculation (*c*) van der Waals coefficients from Kirkwood–Müller formula	3284	−4024	853	113
Our calculation (*d*) van der Waals coefficients from Fowler	3284	−4100	927	111
Lennard-Jones and Taylor r^{-11} force of repulsion	3194	−1832	—	1362
de Boer and Verwey's values of b and ρ but no van der Waals terms	3206	−2687	—	519
Exponential repulsion with $\rho = 0.345\times10^{-8}$ and van der Waals coefficients as in (*c*)	3206	−3150	829	885

**Values of r_0, ρ, etc. are those given in Table II.*

(*c*) Evaluated from the Kirkwood–Müller formula (14), using, in addition to the polarizabilities referred to above, the diamagnetic susceptibilities of the ions calculated by Slater's method as has been recommended by Myers (16).

(*d*) Taken from the table compiled by Fowler (8).

See Table I for numerical values of these coefficients.

The particular choice made caused some variation of the constant ρ deduced from compressibility data. It should be noted that whatever method was utilized to obtain the van der Waals coefficients, the contribution to the cohesive energy obtained by us was greater than the values recorded by Mayer and Maltbie (15) and by de Boer and Verwey (7). We have not been able to ascertain the source of their values.

Results are recorded in Tables II and III. The choices made in dealing with the van der Waals term are indicated, as well as the parameters of the crystal which were employed. Both our computations and those of earlier workers have been summarized. Where individual terms are given which were not stated in the work of the original authors, these were evaluated by us from their publications.

DISCUSSION

Attention should be drawn to the range of values which may be obtained for the surface energy of magnesium oxide due both to the choice of the function employed for the energy of repulsion and to the values selected for the van der Waals attractive terms. These choices are of minor importance in the case of the cohesive energy, but are of extreme importance in the case of the surface energy.

The results raise the general question whether or not the use of the Born-Mayer model is justified to calculate the surface energy of ionic crystals, or whether the discrepant results are due to its inadequacy in the special case of magnesium oxide. Brill, Hermann, and Peters (6) have stated on the basis of X-ray measurements of electron density that magnesium oxide is not completely ionic in character in the solid state. They support their contention by reference to the work of de Boer and Verwey (7), in which the electron affinity of O is calculated for the series of alkaline earth oxides, by means of cohesive energies and the Born cycle. It is pointed out that the oxides of beryllium and magnesium have high values of the electron affinity when determined in this way. It should be noted, however, that these values are based upon the use of $\rho = 0.345 \times 10^{-8}$, which, as has been pointed out above, may lead to erroneous results. The experimental evidence must be recognized, however, and since de Boer and Verwey also point out that the bond in the gaseous magnesium oxide molecule is quite covalent in character, the treatment of the problem by a model assuming complete ionic character may not be justified. This does not, however, explain the wide variations in the computed values which are recorded in Table III. These arise from changes in the assumed values of the coefficients, changes which did not materially affect the cohesive energy. The results emphasize the sensitivity of calculated values of surface energy to the details of computation. They also suggest that the agreement between the Lennard-Jones and Taylor result and the experimental value of Jura and Garland may be fortuitous. The result obtained by Jura and Garland is of a preliminary nature as the authors have stressed (11) and the general procedure must be carefully assessed as Bauer (2) has emphasized. It would therefore seem that further experimental data are urgently required, and that some caution must be exercised in the use of calculated values until experimental results have been accumulated.

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THE PREPARATION OF L-SORBOSE FROM 5-*KETO*-D-GLUCONIC ACID (L-SORBURONIC ACID)[1]

By J. K. N. Jones[2] and W. W. Reid[3]

ABSTRACT

L-Sorbose has been prepared from 5-*keto*-D-gluconic acid.

INTRODUCTION

The most convenient method of preparation of L-sorbose is undoubtedly from the biochemical oxidation of sorbitol (1). The purpose of this communication is to demonstrate how D-glucose can be converted to L-sorbose by purely chemical transformations. The starting product was the calcium salt of 5-*keto*-D-gluconic acid (L-sorburonic acid) which had been prepared by biochemical oxidation of D-glucose (4). Salts of this acid can be prepared by prolonged oxidation of D-glucose with bromine (3) or electrolytically (2). When the calcium salt was shaken with methanolic hydrogen chloride it dissolved with the formation of a mixture of products composed mainly of the methyl glycoside methyl ester of 5-*keto*-D-gluconic acid. The carbomethoxy group of this glycoside was reduced with sodium borohydride to the alcohol with the formation of methyl L-sorbofuranoside from which L-sorbose was prepared by hydrolysis.

Since the oxidation of sugars by bromine water to 5-*keto*hexonic acids is a general reaction (3) the interconversion of aldoses to ketoses with concomitant inversion of the chain of hydroxyl groups becomes possible.

EXPERIMENTAL

Solutions were evaporated under reduced pressure. Optical rotations were measured in water at 20°±2° (unless otherwise stated). Sugars were separated chromatographically in either (*a*) ethyl acetate – acetic acid – formic acid – water (18:3:1:4, v/v) or (*b*) *n*-butanol–water–pyridine (18:3:3, v/v), and detected with the *p*-anisidine–hydrochloride spray.

Methyl 5-keto-D-Glucofuronic Acid Methyl Ester

The calcium salt of 5-*keto*-D-gluconic acid hydrate ($2\frac{1}{2}$, H_2O) (22 gm.) was suspended in methanol (500 ml.) and hydrochloric acid (d. 1.12, 20 ml.) added. The mixture was stirred overnight when a clear solution resulted. The pale yellow reaction mixture was heated at 40°C. for 24 hr., cooled, and then passed down columns of Amberlite resin 1R120 and 1R4B, which had been washed previously with dry methanol. The effluent was concentrated to a sirup (17 gm.) which was dissolved in acetone and filtered from insoluble material. The resultant methyl ester methyl glycoside was obtained as a pale yellow

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Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario and Research Department, H. W. Carter and Company Limited, Coleford, Gloucester, England.
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non-reducing sirup (14.2 gm.) $[\alpha]_D$ −24° (*c*, 3.6 in MeOH). Found: OMe, 28.1%. Calc. for $C_8H_{14}O_7$: OMe, 27.9%. The product contained three components, detected chromatographically, which moved, relative to rhamnose (R_{RH}), at the rates 1.25, 1.59, and 1.98 (solvent (*b*)). They gave yellow orange spots with the *p*-anisidine spray. The fastest moving material was present in traces only. 5-*keto*-D-Gluconic acid had R_{RH} 0.95 in solvent (*a*).

Methyl L-*Sorbofuranoside and* L-*Sorbose*

The methyl ester methyl glycoside (2 gm.) was dissolved in water (10 ml.) and sodium borohydride (0.5 gm.) added. The solution became warm and changed color from pale yellow to pale green. After 24 hr., excess of acetic acid was added and the solution was deionized on Amberlite resins 1R120 and 1R4B. On concentration a sirup (1.28 gm.) remained which contained five components. These materials moved on the chromatogram relative to rhamnose at the rates 0.38, 0.91, 1.07, 1.87, and 2.12 (solvent (*b*)). The slowest moving component which reduced Fehling's solution was identified as sorbose, and results probably from the hydrolytic action of the acidic resin on the methyl furanoside. The components with R_{RH} 0.91 and 1.07 behaved like methyl sorbofuranoside whilst the fastest two components which were present in trace amounts only were not identified. The mixture was heated with *N* sulphuric acid for three hours at 100°C., cooled, neutralized ($BaCO_3$), and filtered. The filtrate on concentration gave crystalline L-sorbose, which was recrystallized from methanol. The product (0.71 gm.) had m.p. 165°C. not depressed on admixture with an authentic specimen, moved on the chromatogram at the same rate as sorbose, and had $[\alpha]_D$ −41° (*c*, 1.1). Found: C, 40.1; H, 6.9%. Calc. for $C_6H_{12}O_6$: C, 40.0, H, 6.7%.

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MERCURY PHOTOSENSITIZED DECOMPOSITION OF ETHYLENE OXIDE[1]

By R. J. Cvetanović

ABSTRACT

Some aspects of the mercury photosensitized decomposition of ethylene oxide at room temperature have been reinvestigated. At least two, and probably more than two, distinct primary steps occur. The previously assumed major primary formation of hydrogen by a molecular process is shown to occur to a relatively small extent only. Hydrogen atoms play an important role in the process, as well as the following radicals: CH_3, CHO, CH_2CHO, and C_2H_5, and probably to a lesser extent also CH_2. The products formed are CO, H_2, C_2H_6, a little CH_2CO and C_2H_4, and large amounts of aldehydes. The presence of higher aldehydes has been demonstrated. While there is a general similarity to the other modes of decomposition of ethylene oxide, a unique and unambiguous solution of the complete reaction mechanism is at present not possible.

In a previous publication (5) an investigation of the reaction of oxygen atoms with ethylene has been reported. The primary step of the readily occurring reaction is believed to be a direct addition of the oxygen atom to the double bond in ethylene. Very little or no ethylene oxide is found, however, and a variety of products is formed instead, presumably as a result of further reactions of the initially produced energy rich molecule

$$C_2H_4+O \rightarrow C_2H_4O^* \qquad [1]$$
$$C_2H_4O^* \rightarrow \text{products.}$$

A support for this view is found in the similarity of the products formed in this process with those reported in the literature for the thermal, photolytic, and mercury photosensitized decomposition of ethylene oxide. All these processes appear to be quite complex and are difficult to treat in an unambiguous manner. While their courses cannot be expected to be identical, the over-all similarity suggests that a comparative study may yield useful information regarding the more important features of the respective mechanisms.

An investigation of the mercury photosensitized decomposition of ethylene oxide was reported in 1948 by Phibbs, Darwent, and Steacie (12). The observed products were CO, H_2, CH_3CHO, and a polymer, as well as smaller amounts of CH_4, HCHO, and of a fraction indicated as "C_2 hydrocarbons" but not further analyzed. It was postulated that initially an energy rich ethylene oxide molecule was formed and that it was capable of isomerizing to acetaldehyde or splitting in the following manner

$$C_2H_4O^* \rightarrow H_2+CO+CH_2. \qquad [2]$$

Only a small portion of the primary process was considered to proceed by the reaction

$$C_2H_4O+Hg^* \rightarrow C_2H_3O+H+Hg \qquad [3]$$

(Hg* refers to Hg $6(^3P_1)$ atoms). All the hydrogen is, therefore, supposed to

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be formed by a molecular process and a very minor role is ascribed to hydrogen atoms.

Direct photolysis of ethylene oxide in the far ultraviolet was reported in 1950 by Gomer and Noyes (8). The products formed were CO, H_2, CH_4, C_2H_6, smaller amounts of HCHO and CH_3CHO, and almost certainly some C_2H_5CHO. The authors were led to assume for the primary step the reaction

$$C_2H_4O+h\nu \rightarrow CH_3+HCO \qquad [4]$$

followed by (or simultaneous with)

$$HCO \rightarrow H+CO. \qquad [5]$$

A considerable amount of work has been done on thermal decomposition of ethylene oxide. A recent investigation was conducted by Lossing, Ingold, and Tickner (10) who were able to observe directly by a mass spectrometer the products of the pyrolysis at 800 to 1000°C. They found CO, H_2, CH_4, C_2H_6, CH_2CO, and an abundant formation of methyl but no methylene radicals. Propane, formaldehyde, and acetaldehyde, reported previously at lower temperatures, were not formed. Mueller and Walters (11) found that at 400°C. acetaldehyde, ketene, and some formaldehyde were formed but not propionaldehyde, at least not in amounts comparable to those of acetaldehyde.

Both Lossing and his co-workers and Mueller and Walters find it necessary to ascribe an important role in the thermal decomposition of ethylene oxide to the primary splitting into CH_3 and HCO, analogous to the reactions [4] and [5] proposed by Gomer and Noyes, and to abandon the classical view of a primary formation of methylene radicals and formaldehyde. The well-known use of ethylene oxide as an excellent source of methyl radicals is thus made more easily understandable. In the reaction of oxygen atoms with ethylene the products formed (CO, paraffinic aldehydes, H_2, CH_4, C_2H_6, C_3H_8, and probably some CH_2CO) suggest a somewhat similar mode of decomposition of the initially formed intermediate. The mechanism proposed for the mercury photosensitized decomposition, on the other hand, is very different. The present work has been carried out, therefore, in order (1) to obtain further information on products formed in the mercury photosensitized decomposition of ethylene oxide, (2) to test the postulated molecular production of hydrogen and other features of the previously proposed mechanism, (3) to attempt to correlate the main features of this process with the other modes of decomposition of ethylene oxide, and (4) to attempt, by analogy, to formulate the more important of the secondary reactions following the addition of oxygen atoms to ethylene.

EXPERIMENTAL

The reaction was studied at room temperature using a conventional type of apparatus, including a cylindrical quartz reaction vessel (5 cm. in diameter, 10 cm. long). The apparatus and the analysis of products have been described in detail previously (3, 5).

Ethylene oxide was obtained from Matheson Co., Inc., ethylene was supplied by Ohio Chemicals Canada, Ltd., and butene-1 was a Phillips reagent grade

product. All the three reagents were further purified by repeated bulb to bulb distillation *in vacuo*. Deuterated ethylene oxide was kindly supplied by Dr. D. J. Worsfold of these laboratories.

The quantum yields of reaction products were determined relative to the formation of hydrogen by mercury photosensitized decomposition of 200 mm. of *n*-butane, and taking 0.50 for the value of ϕH_2, as found by Bywater and Steacie (1).

RESULTS

The pressure dependence of the quantum yields of formation of some of the products in the mercury sensitized decomposition of ethylene oxide is shown in Fig. 1. The trends in the H_2, CO, and CH_4 formation are in agree-

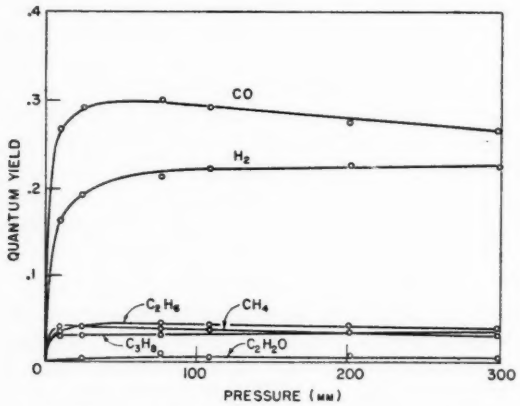

FIG. 1. Pressure dependence of the quantum yields of formation of some of the products in the mercury photosensitized decomposition of ethylene oxide (static experiments, exposure 90 min., mean $I_a = 3.27 \times 10^{13}$ quanta sec.$^{-1}$).

ment with those established by Phibbs, Darwent, and Steacie (12). The "C_2 fraction" reported by these authors is seen to consist mainly of C_2H_6 and C_3H_8. Small amounts of ketene (identified and estimated by mass spectrometer) are separated out with the propane. In addition very small amounts of C_4H_{10} are usually found with the propane and there is indication that traces of ethylene accompany ethane. In this series of experiments no determinations of aldehydes nor of ethylene oxide consumption were attempted. Determinations of these quantities were reported previously (12).

The effect of the addition of very small amounts of ethylene to ethylene oxide is shown in Table I for static (*A*) and circulating (*B*) experiments and for the latter also in Fig. 2. The inhibiting effect of ethylene is extremely pronounced; hydrogen production is strongly suppressed and to a somewhat smaller extent the production of carbon monoxide and methane. On the other hand, the amount of propane formed is much increased. The figures for ethane are uncertain since small amounts of this compound were determined

TABLE I

THE INHIBITING EFFECT OF ETHYLENE
(Exposure 90 min.)

Run	C_2H_4O, mm.	Mean C_2H_4/C_2H_4O	Quantum yields						
			CO	H_2	CH_4	C_2H_6	C_3H_8	$H_2-C_2H_2$	$-\Delta C_2H_4$
A. Static experiments (mean $I_a = 2.95 \times 10^{15}$ quanta sec.$^{-1}$)									
49	200.0	—	.278	.217	.034	.043	.043	Not detd.	Not detd.
48	199.2	.00567	.149	.046	.012	.010	.083	Not detd.	Not detd.
45	201.1	.0160	.121	.028	.015	.022	.078	Not detd.	Not detd.
47	199.3	.0206	.109	.026	.013	.014	.083	Not detd.	Not detd.
43	200.0	.0285	.104	.025	.012	.021	Not detd.	Not detd.	Not detd.
44	201.2	.0336	.099	.022	.012	.014	.067	Not detd.	Not detd.
B. Circulating experiments (mean $I_a = 3.27 \times 10^{15}$ quanta sec.$^{-1}$)									
8	99.8	—	.284	.220	.043	.048	.037	.220	—
11	199.0	.00261	.170	.053	.021	.051	.075	.051	.307
10	198.5	.00584	.146	.036	.019	.051	Not detd.	Not detd.	.329
12	198.0	.0122	.131	.029	.017	.043	.075	.023	.342
9	100.9	.0432	.096	.042	.011	.032	.050	.027	Not detd.

in the presence of excess ethylene. Large amounts of ethylene are consumed in the process. Determination of eventual butane formed proved not to be feasible in the presence of a huge excess of ethylene oxide. For this reason a

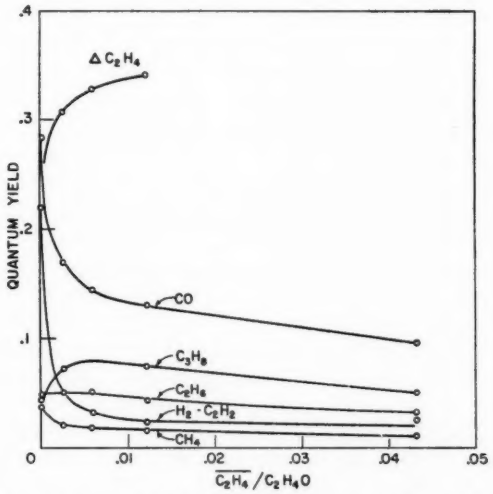

FIG. 2. The inhibiting effect of ethylene (circulating experiments, exposure 90 min., mean $I_a = 3.27 \times 10^{15}$ quanta sec.$^{-1}$).

series of experiments was performed using butene-1 instead of ethylene as the inhibitor. The results are presented in Table II and the effect shown is very

TABLE II

EFFECT OF ADDITION OF BUTENE-1 TO 100 MM. OF ETHYLENE OXIDE
(Mean $I_a = 3.67 \times 10^{15}$ quanta sec.$^{-1}$)

Run	C_4H_8-1, mm.	Irradn. time, min.	Quantum yields							
			CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	Total RCHO	Room temp. fraction
2	—	90	.291	.222	.037	.043	Trace	.039	Not detd.	Very small
74	2.8	100	.138	.033	.021	.020	.044	.001	.175	Not detd.
75	2.4	150	.155	.038	.023	.021	.034	Not detd.	.225	Not detd.
76	5.5	150	.100	.022	.017	.018	.030	Trace	.178	.14
78	5.2	150	.100	.021	.017	Not detd.	Not detd.	Not detd.	Not detd.	.13[a]

[a] *Composed mainly of higher saturated aldehydes (propanal to hexanal) and octane (probably 3,4-dimethylhexane).*

much the same as with ethylene. The following distinctions, however, are to be noted: propane is nearly completely suppressed, appreciable amounts of ethylene are produced, and appreciable quantities of less volatile substances ("room temperature fraction") are formed. By a combination of mass-spectrometer analysis and the removal of the aldehydes by polymerization on solid KOH, this fraction is found to be quite complex, being composed mainly

TABLE III

PRODUCTS OF MERCURY SENSITIZED DECOMPOSITION OF 100 MM. OF ETHYLENE OXIDE ALONE AND OF 100 MM. OF ETHYLENE OXIDE WITH 3.45 MM. ETHYLENE ADDED
(Mean $I_a = 4.93 \times 10^{15}$ quanta sec.$^{-1}$, 25±1°C.)

Run	Irradn. time, min.	Mean C_2H_4, mm.	Quantum yields							
			CO	H_2	CH_4	C_2H_6	C_3H_8	CH_2CO	H_2–C_2H_2	RCHO
A. Ethylene oxide alone										
55	30	—	.287	.217	.044	.048	.030	.010	.217	.169
59	60	—	.295	.223	.043	.044	.027	.016	.223	.166
53	90	—	.294	.226	.041	.042	.026	.008	.226	Not detd.
61	90	—	.297	.224	.041	.040	Not detd.	Not detd.	.224	.139
57	120	—	.295	.216	.042	.041	.026	.009	.216	.084
B. Ethylene oxide+ethylene										
56	30	3.18	.118	.039	.015	.043	.043	.024	.025	.248
60	60	3.02	.120	.045	.012	.046	.046	.026	.027	Not detd.
54	90	2.84	.129	.042	.014	.044	.045	.021	.027	.236
58	120	2.71	.132	.040	.015	.038	.045	.020	.027	.225

of higher paraffinic aldehydes (propanal to hexanal) and of higher paraffins (up to octane).

In order to establish in greater detail the effect of ethylene addition on the formation of various products, alternate experiments were performed with 100 mm. of ethylene oxide alone and 100 mm. of ethylene oxide with 3.45 mm. ethylene added. The time of exposure was varied and the results are given in Table III. In addition to the already indicated suppression of H_2, CO, and CH_4, and the increase of C_3H_8 production on addition of ethylene, it is also seen that ketene and especially aldehyde formation is much increased. Aldehyde was determined by infrared absorption measurement on the basis of calibrations with acetaldehyde (in the presence of analogous quantities of ethylene oxide). The quantities for aldehyde obtained in this manner are approximate because besides acetaldehyde its higher homologues appear to be present in quite appreciable quantities. This was evident from the details of the infrared absorption spectra and also from a partial separation, by the use of gas–liquid partition chromatography (2), of some higher aldehydes from the huge excess of ethylene oxide and their subsequent identification by mass spectrometer. A few determinations of HCHO were made in the manner described previously (5). Only very small amounts of this substance were found. There might have been, however, an appreciable loss of this compound by polymerization.

The inhibiting effects of C_2H_4 and C_4H_8-1 indicate that in the uninhibited reaction most of the hydrogen is formed through action of hydrogen atoms. In the inhibited reaction hydrogen production is not completely suppressed, suggesting that it may be formed by a molecular rather than an atomic process. In order to test this possibility several experiments were carried out with mixtures of C_2H_4O and C_2D_4O. The results are given in Table IV. In the uninhibited reaction (run 64) such mixtures form large amounts of HD, while in the inhibited reaction (runs 62 and 61) HD is suppressed to the level that appears when C_2D_4O is used in the absence of C_2H_4O (runs 63 and 65). In the inhibited reaction, therefore, hydrogen is formed by a molecular process. The interpretation of the ratios of the isotopic methanes formed is somewhat more difficult because the figures for CH_3D and CH_4 may be subject to large errors. The ratios CD_4 to CD_3H should, on the other hand, be accurate and the indications are that both in the inhibited and uninhibited reaction, methane is probably formed predominantly, but possibly not entirely, from free methyl radicals.

It is of interest also that there are pronounced isotopic effects in the rates of hydrogen formation, both the abstraction and the molecular formation of deuterium taking place less readily than those of hydrogen. This is in agreement with the observations of other workers in abstractions of the two isotopes of hydrogen and explains the fact that in the uninhibited decomposition of the 1:1 C_2D_4O–C_2H_4O mixture (run 64) the relative rate of HD formation is not as large as would be expected on probability grounds. An isotopic effect in a molecular reaction has recently been found in the mercury photosensitized decomposition of ethylene (6).

TABLE IV

EXPERIMENTS WITH C_2H_4O AND C_2D_4O
(Mean $I_a = 2.34 \times 10^{15}$ quanta sec.$^{-1}$)

Run	Initial pressures (mm.)				Irradn. time, min.	Quantum yields									
	C_2H_4O	C_2D_4O	C_2H_4	C_4H_8-1		CO	Total H_2	Total methane	H_2	HD	D_2	CD_4	CD_3H	CH_3D	CH_4
49	200	—	—	—	90	.278	.217	.034	.217	—	—	—	—	—	.034
64	100	100	—	—	120	.259	.168	.026	.075	.071	.022	.008	.007	.004	.007
43	200	—	6.3	—	90	.104	.025	.012	.025	—	—	—	—	—	.012
62	100	100	5.4	—	300	.116	.022	.012	.014	.003	.005	.004	.003	.0015	.005
57	100	—	—	—	120	.295	.216	.042	.216	—	—	—	—	—	.042
65	—	100	—	—	120	.229	.088	.037	—	.004	.084	.032	.005	—	—
63	—	100	—	5.6	240	.066	.012	.012	.001	.003	.008	.007	.004	.0004	.0005
61	50	50	—	5.4	150	.099	.021	.014	.012	.0031	.0055	.003	.003	.002	.006

DISCUSSION

The quenching efficiency of ethylene is 10 times greater than that of ethylene oxide (4) and even for the largest ratios of ethylene to ethylene oxide used in the present experiments the fraction of the exciting radiation quenched by ethylene is small and cannot be responsible for the large inhibiting effects observed. It appears safe to conclude that the inhibition is due to the addition of H-atoms to ethylene or butene-1. In the former case the increased ethyl radical concentration leads to an increased propane formation, by combination with methyl radicals, which also leads to some decrease in methane formation. With butene-1 propane is not formed at all, but higher paraffins instead. The experiments with butene-1 show that quite appreciable amounts of ethylene are formed in the decomposition of ethylene oxide but, in the absence of excess butene, H-atoms add on to it readily; the ethyl radicals thus formed explain the production of propane in the "uninhibited" reaction.

An inspection of the magnitude of the inhibiting effect produced by ethylene and of the large consumption of this compound shows that large quantities of H-atoms are formed in the sensitized decomposition of ethylene oxide. This finding rules out the previously suggested (12) formation of hydrogen by a molecular process as the major primary step. The amounts of CH_4, C_2H_6, and C_3H_8 produced indicate that substantial quantities of methyl radicals are also formed. Formation of methane at room temperature by abstraction of hydrogen indicates that a relatively loosely bound hydrogen atom is available. All these considerations point to a primary step of the type suggested by Gomer and Noyes (8) for the direct photolysis: primary production of CH_3 and HCO radicals, the latter readily decomposing into H and CO. In order to explain the formation of higher aldehydes it is then necessary to assume also the occurrence of the reactions

$$R+HCO\ (+M) \rightarrow RCHO\ (+M) \qquad [6]$$

in addition to

$$R+HCO \rightarrow RH+CO \qquad [7]$$

and

$$H+HCO \rightarrow H_2+CO. \qquad [8]$$

The major features of the process are then qualitatively readily explainable. When ethylene is added, reaction [8] is suppressed and at the same time large quantities of C_2H_5 are formed which, through an increase in aldehyde formation, lead to more rapid removal of HCO radicals and therefore their decreased decomposition to yield CO. Thus, a drastic suppression of H_2, partial suppression of CO, and a large increase in aldehydes is observed. A slight pressure dependence of reaction [6] could explain the pressure dependence of CO formation. Alternately, there may be a slight collisional deactivation of an initially produced excited ethylene oxide molecule. The very slight increase in the yield of hydrogen with increasing pressure may be due to pressure dependence of reaction [5], as suggested by Horner, Style, and Summers (9).

It would appear, on the basis of the foregoing conceptions, that H-atoms undergo preferentially reaction [8], CH_3 radicals both reactions [6] and [7], and C_2H_5 and any higher radicals predominantly reaction [6]. These differences

may be due to different availability of degrees of freedom for a distribution of the heat of the reaction. It should be pointed out at the same time that a combination of CH_3 and CHO radicals to give acetaldehyde is, on the basis of the existing experimental information, indistinguishable from a direct primary isomerization to this compound without decomposition. The formation of higher aldehydes, on the other hand, would seem to require the occurrence of reactions [6].

While a primary split into CH_3 and CHO may explain in a qualitative way the major features of the process, it is evident that at least one more primary process has to be considered. The experiments with mixtures of C_2H_4O and C_2D_4O show that a small fraction of hydrogen is formed by a primary molecular process possibly by reaction [2] or by the similar reaction

$$C_2H_4O^* \rightarrow H_2+CH_2CO. \qquad [9]$$

It appears, therefore, to be reasonably certain that there are at least two primary processes. A primary molecular formation of methane, if it occurs at all, does not seem to be very important. A primary split into H-atoms and C_2H_3O radicals, (reaction [3]), on the other hand, is very likely in view of the seemingly largely saturated character of the ethylene oxide molecule. The properties of the C_2H_3O radicals have been investigated by Gomer and Noyes (8) and it appears that there is about equal probability of decomposition of these radicals into CH_3 and CO and of their stabilization by isomerization, presumably to CH_2CHO radicals. The latter could then lead to aldehyde formation. It can be seen that the qualitative consequences of such a primary step, followed by a number of feasible secondary reactions, are similar to those of a primary split into CH_3 and HCO. Attempts to exclude the latter primary step, however, lead to quantitative difficulties. Complete and unambiguous stoichiometric and kinetic treatment is at present impossible because of the lack of detailed quantitative information on the aldehydes formed and a very limited knowledge of the relative values of rate constants of the different reactions involved. Some conclusions, on the other hand, can be drawn from a comparative analysis of the various modes of decomposition of ethylene oxide.

The stoichiometry of the reaction of oxygen atoms with ethylene (5) can be approximately represented by

$$\begin{aligned} O+1.38\ C_2H_4 \rightarrow\ & .50\ CO+.15\ CH_3CHO+.20\ C_2H_5CHO+.05\ C_3H_7CHO \\ & +.03\ C_2H_4O+.04\ CH_2CO+.09\ H_2+.11\ CH_4 \\ & +.17\ C_2H_6+.17\ C_3H_8+.03\ (C_2H_4O\text{-polymer}). \end{aligned}$$

A stoichiometric balance of the likely processes involved can be written as follows:

$$O+C_2H_4 \rightarrow C_2H_4O^* \rightarrow \begin{cases} .03 \text{ polymer} \\ .03\ C_2H_4O \\ .05\ H_2+CH_2+CO \\ .04\ H_2+CH_2CO \\ .10\ H+C_2H_3O \\ .75\ CH_3+HCO \end{cases}$$

$$.10\ C_2H_3O \rightarrow .05\ CH_2CHO + .05\ CH_3 + .05\ CO$$
$$.05\ CH_2 + .05\ CH_3 \rightarrow .05\ C_2H_4 + .05\ H$$
$$.32\ CH_3 \rightarrow .16\ C_2H_6$$
$$.11\ CH_3 + .11\ HCO \rightarrow .11\ CH_4 + .11\ CO$$
$$.17\ CH_3 + .17\ C_2H_5 \rightarrow .17\ C_3H_8$$
$$.15\ CH_3 + .15\ HCO \rightarrow .15\ CH_3CHO$$
$$.28\ HCO \rightarrow .28\ H + .28\ CO$$
$$.43\ H + .43\ C_2H_4 \rightarrow .43\ C_2H_5$$
$$.20\ C_2H_5 + .20\ HCO \rightarrow .20\ C_2H_5CHO$$
$$.01\ C_2H_5 + .01\ HCO \rightarrow .01\ C_2H_6 + .01\ CO$$
$$.05\ C_2H_5 + .05\ CH_2CHO \rightarrow .05\ C_3H_7CHO.$$

The proposed scheme involves some simplifications and for some of the steps alternative reactions may be written. The small primary split into H and C_2H_3O, in particular, is suggested only in order to explain the formation of C_3H_7CHO and may prove to be unnecessary if this compound is found to arise by some other type of radical combination. Regardless of these uncertainties, in its main outline, the scheme appears feasible on the basis of the present knowledge. Considering the reactions

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [10]$$
$$CH_3 + CHO \rightarrow CH_4 + CO \qquad [11]$$
$$CH_3 + CHO \rightarrow CH_3CHO \qquad [11']$$

and

$$CHO \rightarrow H + CO \qquad [5]$$

it is likely that reactions [11] and [11′] have each a collision efficiency of about 0.5. Assuming that (1) the collision efficiency of reaction [10] is unity and of reaction [11] 0.5, (2) the collision diameters of CH_3 and HCO have the same value of 3.5 Å, (3) the effective reaction volume is 10 cc., and (4) $k_5 = 10^{13} \exp(-E_5/RT)$, a value of 14.4 kcal./mole can be calculated for E_5 from the observed rate of reaction [10] and the ratio of the rates of reactions [5] and [11] as given in the foregoing stoichiometric balance (.28/.11). Even with an ample allowance for uncertainties in the assumptions made, E_5 remains within the range of the values for the same quantity quoted in the literature (13).

Inasmuch as the primary decomposition of ethylene oxide in the mercury photosensitized reaction follows the same course, the relative amounts of the products formed when ethylene is present should be very much the same as in the reaction of O-atoms with ethylene. A comparison of the rates of formation of all but some of the minor products detected is given in Table V. The figures given should be regarded as approximate since there is an appreciable uncertainty in some of the analytical results, particularly those for the total aldehydes and ketene. Nevertheless, it is clear that there is a broad similarity, as evidenced by the values reduced to equal CO production. There are also some important differences. In the mercury sensitized decomposition of ethylene oxide in the presence of ethylene less fragmentation products (CO, CH_4, C_2H_6, C_3H_8) and more aldehydes are formed, and also, relative to equal CO formation, there is less methane while propane remains about the same. These differences are qualitatively explainable by a decreased initial split into CH_3 and HCO and a considerably increased primary split

TABLE V

COMPARISON OF THE RATES OF FORMATION OF THE MAIN PRODUCTS IN THE MERCURY SENSITIZED DECOMPOSITION OF ETHYLENE OXIDE AND IN THE REACTION OF OXYGEN ATOMS WITH ETHYLENE (For ethylene oxide decomposition the rates are relative to the total number of moles of products containing oxygen, i.e., to the sum of CO, total aldehyde, and CH_2CO; the bracketed figures are relative to CO taken as 0.50. For the reaction of oxygen atoms with ethylene, the rates are expressed per oxygen atom consumed)

	CO	H_2	CH_4	C_2H_6	C_3H_8	CH_2CO	RCHO	C_2H_4
Ethylene oxide alone	.60	.46	.10	.10	.07	.03	.37	Small
Ethylene oxide $+C_2H_4$	.35 (.50)	.07 (.10)	.04 (.16)	.10 (.14)	.12 (.17)	.06 (.08)	.59 (.85)	Not detd.
Ethylene oxide $+C_4H_8$	.34 (.50)	.07 (.10)	.05 (.08)	.06 (.09)	.002 (.002)	.01 (.02)	.65 (.89)	.10 (.15)
O atoms $+C_2H_4$	.50	.09	.11	.17	.17	.04	.40	Not detd.

into H and C_2H_3O radicals. The CH_2CHO radicals, formed from C_2H_3O, could be visualized as being responsible for increased aldehyde formation by combination with free radicals. While this view seems to fit better all the experimental observations, it is also possible that the increased aldehyde formation could be due to a direct primary isomerization to acetaldehyde. An analysis of the material balance of the process, which could remove much of the ambiguity, is impossible until detailed and accurate determinations of the aldehydes formed are available.

An observation arising from the butene-1 inhibited experiments is that some ethylene is formed in the mercury sensitized decomposition of ethylene oxide. Two ways of formation of this compound appear possible: a primary split into C_2H_4 and an O-atom, or some reaction involving CH_2 radicals. In connection with the latter possibility it is of interest that some preliminary work of Gesser (7) indicates that C_2H_4 is formed in the reaction of CH_2 radicals with ethylene oxide.

The results of the experiments reported in the literature and in the present work indicate that there is a significant similarity between the different modes of decomposition of ethylene oxide: the thermal, photolytic, mercury photosensitized, and the decomposition of the energy rich molecule formed in the reaction of oxygen atoms with ethylene. The differences observed appear to be largely of a quantitative rather than a qualitative character and may be ascribed to a variation in the relative importance of the different primary processes and, in the case of thermal decomposition, also to a variation with temperature of the stability and the reactivity of the intermediate free radicals and atoms formed.

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SOLUBILITY CRITERIA FOR THE EXISTENCE OF HYDROXYAPATITE[1]

By J. S. Clark

ABSTRACT

The solubilities of synthetic basic calcium phosphate precipitates in carbon dioxide free aqueous systems were studied over a wide range of conditions. The pH of the suspensions and the calcium and phosphate concentrations in the solutions were determined both after precipitation and after dissolution of the solid phases. Solubility criteria applied to these measurements indicated that hydroxyapatite has a definite solubility product.

INTRODUCTION

Although hydroxyapatite is generally considered to be one of the stable basic calcium phosphates in nature, its existence as a compound with a fixed crystalline form and a unique solubility is controversial. Neumann and his co-workers (6, 7) considered the basic calcium phosphate system to be a solid phase of variable composition so that the principle of solubility product would not apply. In contrast to this opinion, the thermodynamic properties of crystalline hydroxyapatite have been reported by the Chemical Engineering Division of the TVA (8). Since in a previous paper solubility criteria were proposed as a means of establishing the existence of calcium phosphate compounds in soils (2), it was considered desirable to resolve the contrasting views on the solubility of hydroxyapatite in order to evaluate the validity of this approach. The object of the work reported here was to determine whether hydroxyapatite possesses a definite solubility product over a wide range of conditions.

EXPERIMENTAL

The solid phase calcium phosphates used for the solubility measurements were prepared by reacting dilute solutions of $Ca(OH)_2$ and H_3PO_4 at different temperatures for various periods of time while N_2 (CO_2 free) was passed through the systems. Following reaction at elevated temperatures, the flasks containing the suspensions were placed in a water bath at 25°C. for 96 hr. and the pH was measured with a glass electrode in the presence of N_2. The suspensions were filtered rapidly and phosphate and calcium determinations were made on the filtrates by the molybdenum blue (4) and the versene (1) methods, respectively. The activities of the ions were estimated by means of the Debye–Huckel equation (5).

In some cases, the precipitates were separated from the solutions and redispersed at 25°C. in CO_2-free water through which N_2 was passed. After 24 hr., the pH was measured and calcium and phosphate determinations were made on these suspensions in the manner described above.

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RESULTS AND DISCUSSION

In preliminary experiments, it was found that reproducible solubilities could not be obtained in the presence of CO_2 even after reaction for long periods at relatively high temperatures. For this reason, a CO_2-free atmosphere was used in all experiments. In addition, it was found that, although satisfactory results were obtained by rapid mixing of the $Ca(OH)_2$ and H_3PO_4 solutions below a final pH of about 7.8, it was necessary to combine the reacting solutions slowly above this pH in order to obtain equilibrium.

The solubility measurements made on precipitates which had reacted at 90°C. for 120 hr. are reported in Table I, and those obtained by redispersing some of these precipitates in water are presented in Table II. The values for

TABLE I

SOLUBILITY OF HYDROXYAPATITE MEASURED AFTER PRECIPITATION

No.	pH	pCa	pH_2PO_4	pPO_4	$pH-\frac{1}{2}pCa$	$pH_2PO_4+\frac{1}{2}pCa$	$pK_{sp}=10pCa+6pPO_4+2pOH$
1	5.04	2.66	2.24	11.69	3.71	3.57	114.66
2	5.10	2.79	2.48	11.81	3.70	3.88	116.56
3	5.29	2.87	2.50	11.45	3.85	3.94	114.82
4	5.37	3.03	2.65	11.44	3.85	4.17	116.20
5	5.40	3.05	2.55	11.28	3.87	4.08	115.38
6	5.42	2.97	2.54	11.23	3.93	4.03	114.24
7	5.58	3.15	2.77	11.14	4.00	4.35	115.18
8	5.78	3.39	3.02	10.99	4.08	4.72	116.28
9	5.82	3.41	3.05	10.94	4.11	4.76	116.10
10	5.83	3.39	3.04	10.91	4.13	4.74	115.70
11	5.88	3.47	3.15	10.92	4.14	4.89	116.46
12	5.94	3.52	3.11	10.76	4.18	4.87	115.88
13	6.02	3.56	3.33	10.82	4.24	5.11	116.48
14	6.08	3.62	3.27	10.64	4.27	5.08	115.88
15	6.44	3.85	3.58	10.23	4.51	5.51	115.00
16	6.57	4.09	3.49	9.88	4.52	5.54	115.04
17	6.60	4.00	3.71	10.04	4.60	5.71	115.04
18	6.78	4.04	3.97	9.94	4.76	5.99	114.48
19	7.26	4.34	4.70	9.71	5.09	6.87	115.14
20	7.30	4.40	4.77	9.70	5.10	6.97	115.60
21	7.30	4.50	4.69	9.62	5.05	6.94	116.12
22	7.54	4.46	5.17	9.62	5.31	7.40	115.24
23	7.69	4.45	5.43	9.58	5.41	7.66	114.60
24	7.70	4.74	5.17	9.30	5.33	7.54	115.80
25	8.36	4.72	6.60	9.41	6.00	8.96	114.94
26	8.51	4.52	7.20	9.71	6.25	9.46	114.44
27	8.91	5.4*	6.68	8.39	6.21	9.38	114.52

**Approximate Ca^{++} activity.*

TABLE II

SOLUBILITY OF HYDROXYAPATITE MEASURED AFTER DISSOLUTION

No.	pH	pCa	pH_2PO_4	pPO_4	$pH-\frac{1}{2}pCa$	$pH_2PO_4+\frac{1}{2}pCa$	$pK_{sp}=10pCa+6pPO_4+2pOH$
D2	6.31	3.75	3.41	10.32	4.43	5.29	114.80
D6	5.62	3.22	2.85	11.14	4.01	4.46	115.80
D8	6.36	3.90	3.41	10.22	4.41	5.36	115.60
D15	7.13	4.28	4.43	9.70	4.99	6.57	114.74
D20	7.56	4.50	5.05	9.46	5.31	7.30	114.64
D24	6.94	4.28	4.22	9.87	4.80	6.36	116.14
D27	8.48	4.76	6.83	9.40	6.10	9.21	115.04

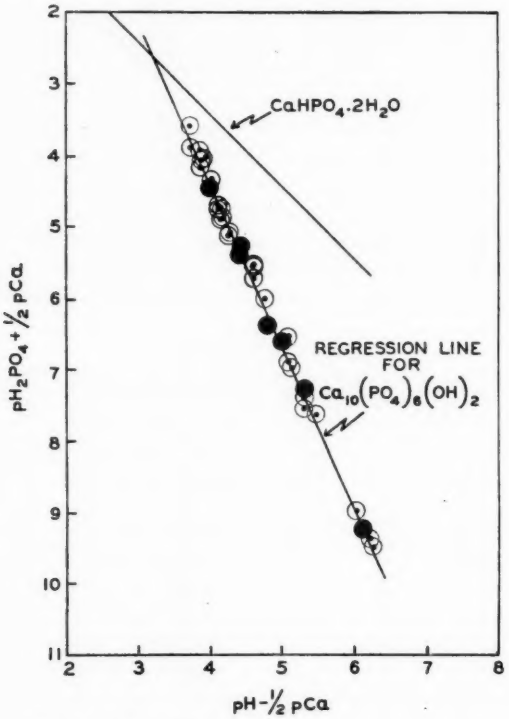

FIG. 1. Solubility diagram.
Legend: ⊙ Solubility measured after precipitation.
● Solubility measured after dissolution.

$pH-\frac{1}{2}pCa$ and $pH_2PO_4+\frac{1}{2}pCa$ in these tables are plotted on the solubility diagram in Fig. 1. Details with respect to the construction and interpretation of the diagram were presented in earlier publications (2, 3). The regression line relating $pH-\frac{1}{2}pCa$ and $pH_2PO_4+\frac{1}{2}pCa$ was calculated from the data and the corresponding value for the negative logarithm of the solubility product was 115.5. The slope of the regression line was similar to that for hydroxyapatite (actual slope 2.26 as compared with a theoretical value of 2.11) indicating that, although the calcium concentration varied from 10^{-3} to 10^{-6} M, the phosphate concentration from 10^{-3} to 10^{-6} M, and the pH from 5 to 9, hydroxyapatite possesses a definite solubility product.

To ascertain if heating to 90°C. for 120 hr. was sufficient to establish equilibrium, solubility measurements were made with precipitates that were prepared by reaction for 24 and 120 hr. at 40°C., 8 and 120 hr. at 60°C., and 4 and 120 hr. at 90°C. The solubilities, measured after equilibration at 25°C., are plotted on the enlarged section of the solubility diagram in Fig. 2. It is seen from Fig. 2 that increasing the reaction temperature decreased the solubilities

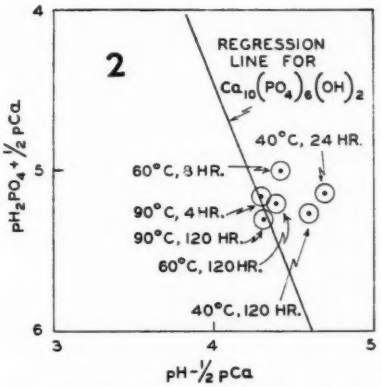

FIG. 2. The influence of reaction temperature and time of reaction at a given temperature on the solubility of hydroxyapatite.

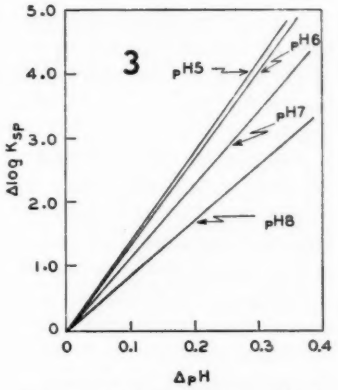

FIG. 3. The effect of errors in the measurement of pH on the calculated solubility product of hydroxyapatite.

of the precipitates. The solubilities were also decreased by increasing the length of the reaction period except at 90°C. The solubility after 4 hr. at 90°C. was as low as that after heating for 120 hr. at this temperature, and it is noted further that the solubility was only slightly higher after heating for 120 hr. at 60°C. Thus, heating for 120 hr. at 90°C. evidently was sufficient to produce stable conditions in these basic calcium phosphate systems.

As it was possible that the systems which had reacted at temperatures below 90°C. were in a state of supersaturation, the precipitates were separated from the solution and dispersed in water at 25°C. and the solubility measured 24 hr. later. The solubilities of precipitates formed at 90°C. were measured in this way and showed good agreement with the values obtained by precipitation (compare Tables I and II). On the other hand, after the solid phase of the system which had reacted for 24 hr. at 40°C. was redispersed in water the value obtained for $pH - \frac{1}{2}pCa$ was 5.14 and that for $pH_2PO_4 + \frac{1}{2}pCa$ was 6.10. Comparing these values with those for the corresponding precipitated system in Fig. 2, it is seen that the solubility did not decrease, indicating that the solution was not simply supersaturated. Similarly, when the other precipitates formed below 90°C. were redispersed in water, the solutions remained at the same degree of apparent supersaturation as in the original precipitated system. Increasing the reaction temperature and the length of the reaction period apparently served to age the precipitates producing better defined crystals with a lower solubility. Although the rate of precipitation and aging of hydroxyapatite is slow, its rate of dissolution is rapid since stable conditions were reached in 24 hr. when the precipitates were dispersed in water. These experiments on the dissolution of hydroxyapatite support the contention that a state of virtual equilibrium had been attained by heating to 90°C., and they indicate that the nature of the solid phase was not changed by heating.

In the light of these experiments on the effect of reaction time and temperature on the solubility of hydroxyapatite, it is improbable that the variability of the solubility products reported in the last columns of Tables I and II was caused by the failure to obtain stable conditions. The variability can be attributed to a great extent to the influence of analytical errors in the calculation of the solubility product where the ion activities are raised to such high exponents. As illustrated in Fig. 3, relatively small errors in pH may have a marked effect on the value of the calculated solubility product. Considering the effect of possible errors in the measurement of pH, the discrepancies observed in the pK_{sp} values do not appear serious.

In these unbuffered systems, errors in the measurement of pH coupled with errors in the determination of calcium and phosphate concentrations were probably sufficient to account for the observed differences in the values obtained for the solubility products. Further refinements in experimental technique would be necessary to obtain an accurate experimental value but these experiments were adequate to demonstrate that, within accountable errors, hydroxyapatite has a definite solubility product over a wide range of conditions.

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PERIODATE–PERMANGANATE OXIDATIONS

I. OXIDATION OF OLEFINS[1]

By R. U. Lemieux[2] and E. von Rudloff[3]

ABSTRACT

It was discovered that olefinic double bonds are readily oxidized in an aqueous solution of periodate which contains only catalytic amounts of permanganate. The data suggest that in the effective pH range of 7 to 10 the permanganate is not reduced at once beyond the manganate state and that it is regenerated from this state by periodate action. Evidence was obtained that the main course of the oxidation of an olefin of type —CH=CH— involves first permanganate oxidation to hydroxyketones which are then rapidly cleaved by periodate to products which may subsequently be oxidized by the permanganate.

INTRODUCTION

The use of a mildly alkaline solution of periodate containing permanganate as a reagent for the detection of carbohydrates on paper chromatograms was described by Lemieux and Bauer (6). This communication deals with the ability of the reagent to oxidize olefins smoothly.

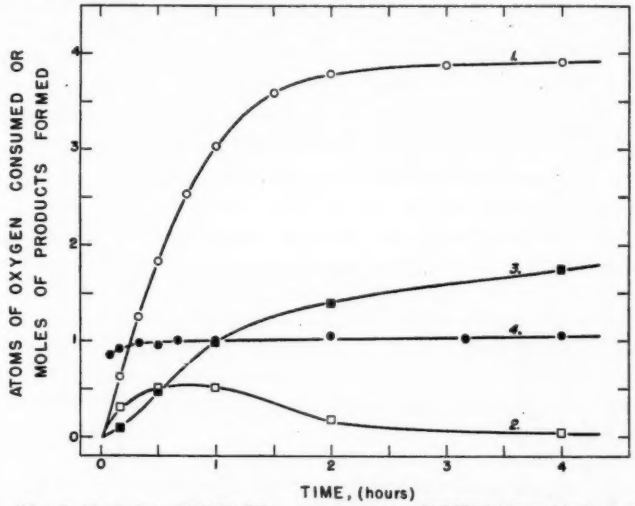

FIG. 1. Plot 1: Periodate (0.0197 *M*) – permanganate (0.00034 *M*) oxidation of oleic acid (0.0025 *M*) in the presence of potassium carbonate at pH 7.7 and 20°C. (atoms of oxygen consumed per oleate ion). Plot 2: Aldehyde formed during the oxidation of oleic acid (plot 1; moles per oleate ion). Plot 3: Acids formed during the oxidation of oleic acid (plot 1; moles per oleate ion). Plot 4: Oxidation of 9,10-dihydroxystearic acid and 9,10-keto hydroxystearic acids under the conditions of plot 1, but without the permanganate (atoms of oxygen consumed per stearate ion).

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The data presented in Fig. 1 (plot 1) show that a reagent consisting of 0.0197 *M* periodate and 0.00034 *M* permanganate at pH 7.7 and 20°C. efficiently oxidized 0.0025 *M* oleate ion with the consumption of the amount of oxidant theoretically required to cleave the olefin to carboxylic acid.

$$\begin{matrix}-CH\\ \|\\ -CH\end{matrix} + 4[O] \longrightarrow 2\,-COOH$$

The fact that after 20 hours' reaction time these conditions gave a product from which azelaic and pelargonic acids were isolated in quantitative yields shows that the oxidation was specific for the olefinic linkage. Periodate alone did not oxidize the olefin. Therefore, the ability of the reagent to bring about complete cleavage of the olefin must depend on an ability of the periodate ions to regenerate permanganate from its reduced state. We have observed that the addition of sodium *meta*-periodate to an alkaline solution of manganate ion (11) resulted in the immediate formation of permanganate ion. This observation provided a satisfactory explanation for the regeneration of the permanganate in the above periodate–permanganate oxidation since Drummond and Waters (2) have recently produced evidence that olefins and other organic compounds do not reduce permanganate at once beyond the manganate stage. This conclusion was supported by the effect of pH on the ability of the reagent to oxidize substances stable toward periodate. The data presented in Fig. 2 show that, in acidic media, the oxidation of mesityl oxide did not go to completion and that the extent of oxidation was least when the pH was lowest. The cessa-

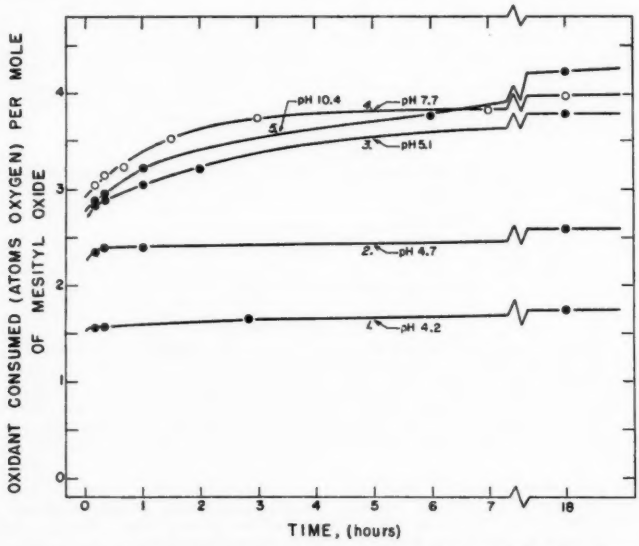

FIG. 2. Experimental rates for the oxidation of mesityl oxide (0.0025 *M*) at 20°C. Relative molar concentrations: mesityl oxide, 1; sodium *meta*-periodate, 7.9; potassium permanganate, 0.13; potassium carbonate, 0 (plot 1), 0.125 (plot 2), 0.25 (plot 3), 1 (plot 4), 10 (plot 5).

tion of oxidation was accompanied by precipitation of manganese dioxide. It is well known that manganate ions disproportionate into manganese dioxide and permanganate ions in acidic media. Since periodate does not oxidize manganese dioxide to permanganate in alkaline media, the oxidations which had ceased to operate in acidic media did not resume when the solution was rendered alkaline. The periodate oxidation of α-glycols usually becomes very slow in strongly alkaline media (1, 10). Since this is a step in the periodate–permanganate oxidation of olefins, high pH's are not favorable. Furthermore, strongly alkaline media lead to disappearance of the typical permanganate color. Therefore, it was concluded that the most favorable pH range for the periodate–permanganate reagent is from 7 to 10.

Permanganate has been widely used to hydroxylate olefins. Treatment of oleic acid with an alkaline solution of permanganate yields racemic *erythro*-9,10-dihydroxystearic acid (3, 5). The reaction results in a green solution containing manganate ion. However, when the oxidation is carried out near neutrality and an excess of permanganate is avoided, the main product is a mixture of 9-keto-10-hydroxy and 9-hydroxy-10-keto-stearic acids (3). 9,10-Dihydroxystearic acid is formed only in smaller amounts. Since King (3) was unable to prepare the ketohydroxy acids by a similar oxidation of the 9,10-dihydroxy acid, it was evident that the mechanism of the permanganate oxidation of olefins is strongly dependent on pH.

The periodate–permanganate oxidation of oleate ion described in Fig. 1 was carried out at pH 7.7, i.e. in the pH range where the main product of the permanganate oxidation of oleate ion is the mixture of ketohydroxy acids. If this product was also intermediate in the periodate–permanganate oxidation, then it could be concluded that the initial stages of the periodate–permanganate oxidation involve true permanganate oxidation. Direct evidence that the ketohydroxy acids were in fact intermediates was obtained by oxidizing oleate ion (0.0025 *M*) at pH 7.7 using a relatively high concentration of permanganate (0.000806 *M*) to speed up the initial stage of the reaction and only a relatively small amount of periodate (0.00106 *M*). The reaction was stopped by the addition of bisulphite at the first indication that the permanganate was not being regenerated as evidenced by the appearance of manganese dioxide. This procedure restricted the reaction to the conditions which prevail in periodate–permanganate oxidation. The product contained the mixture of ketohydroxystearic acids in near quantitative yield based on the amount of periodate added. Elaidic acid was also in part converted to the ketohydroxystearic acids and 10-undecenoic acid was oxidized in part to 10-keto-11-hydroxyundecanoic acid under similar reaction conditions. Since 9,10-epoxystearic acid was not oxidized under these conditions, the intermediate formation of epoxides was ruled out.

Furthermore, the periodate–permanganate oxidation of ethylene resulted in the formation of only about one mole of formaldehyde on the consumption of oxidant equivalent to four oxygen atoms. Had ethylene glycol alone been produced in the first stage of the reaction, a consumption of oxidant equivalent to only two oxygen atoms would have yielded two moles of formaldehyde. Therefore, it seems clear that the periodate–permanganate oxidation of an

olefin in the pH range 7 to 8 has a strong tendency to proceed by way of an acyloin. It is noteworthy in this respect that the permanganate oxidation under near neutral conditions may prove to be a useful means for converting certain olefins to acyloins.

The products isolated after different reaction times in the course of the oxidation of oleate ion under the conditions described in Fig. 1 were analyzed for their aldehyde and carboxylic acid contents. The results, plotted in Fig. 1 (plots 2 and 3), form a picture of the reaction sequences involved in terms of the isolable products. Since periodate alone rapidly oxidized the 9,10-dihydroxy and ketohydroxystearic acids (plot 4), the concentration of these substances must always have been relatively small. The fact that the amount of aldehyde passed through a maximum at 0.52 mole per gram ion of oleate ion oxidized supports the above conclusion that the ketohydroxystearic acids were intermediates in the over-all reaction.

Thus, in terms of the isolable organic products, the periodate–permanganate oxidation can be considered to take place in three stages. The first stage appears to be a complex sequence of reactions which involve permanganate ion in one-electron exchanges leading, near neutrality, mainly to hydroxyketone. The rapid periodate cleavage of the hydroxyketone (and any diol which may have been formed) can be considered as the second stage. This property of the periodate–permanganate reagent is undoubtedly that mainly responsible for the high specificity of the over-all reaction. The oxidation of the products formed in the periodate cleavage through permanganate action can be considered as the third stage. It is noteworthy that the fact that the reagent requires only mildy alkaline conditions is conducive to the oxidation of an aldehyde without degradation.

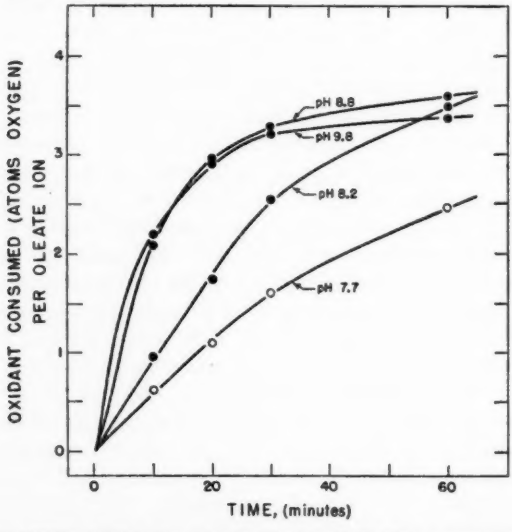

FIG. 3. Effect at 20°C. of pH on the rate of periodate (0.02 *M*) – permanganate (0.00034 *M*) oxidation of oleate (0.0025 *M*).

Although the periodate–permanganate reagent is limited in application to the oxidation of compounds which are soluble in slightly alkaline media, the high yields obtained and the convenience of operation render it likely that the reagent will find application for degradative and analytical purposes. Thus, for example, the oxidation of 10-undecenoic acid gave sebacic acid and formaldehyde in excellent yield. The fact that formaldehyde resisted oxidation suggests the use of the reagent for determining terminal methylene groups (7). The oxidation of mesityl oxide at pH 7.7 gave a quantitative yield of acetone. This result forms a convenient basis for the determination of terminal isopropylidene groups and will be described in a later communication (12).

In view of these possible uses for the reagent, a study was made of the effect of certain variables on the rate of reaction using oleate ion as substrate. The data plotted in Fig. 3 show that the rate of the over-all reaction increases with increase in pH. The effect of temperature on the rate of reaction is illustrated in Fig. 4. The plots of Fig. 5 show clearly that permanganate is involved in the rate controlling stages. The results presented in Fig. 6 show that an increase in the periodate ion concentration has a retarding effect on rate of reaction. This interesting effect was not to be expected. Nevertheless, these results serve as further evidence that in these oxidations the steps which involve periodate ion are fast as compared to those which involve permanganate ion. It should be noted in this respect that the periodate cleavage of glycols is strongly dependent on pH in basic media with the rate of reaction decreasing with increasing pH (1, 10). This fact may account for the slower rate of the second stage of periodate–permanganate oxidation of oleate ion on going from pH 8.8 to 9.8 (see Fig. 3).

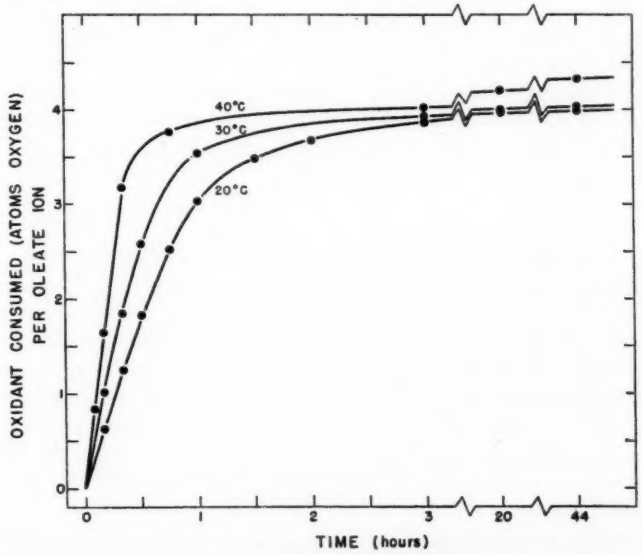

FIG. 4. Effect of temperature on the rate of periodate–permanganate oxidation of oleate using the conditions of Fig. 1, plot 1, except for temperature.

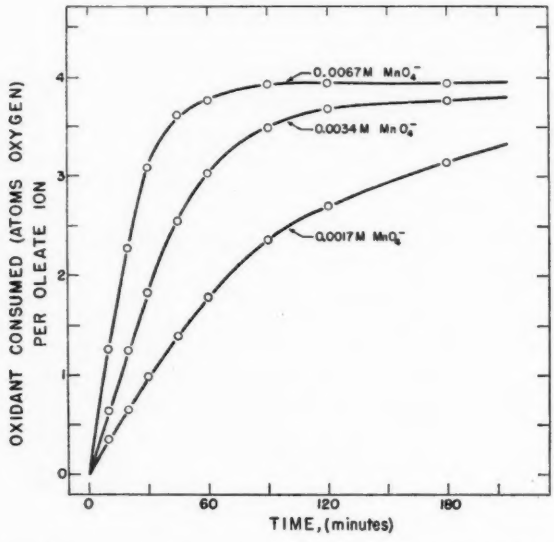

FIG. 5. Effect of the permanganate concentration on the rate of periodate–permanganate oxidation of oleate using the conditions of Fig. 1, plot 1, except for the permanganate concentration.

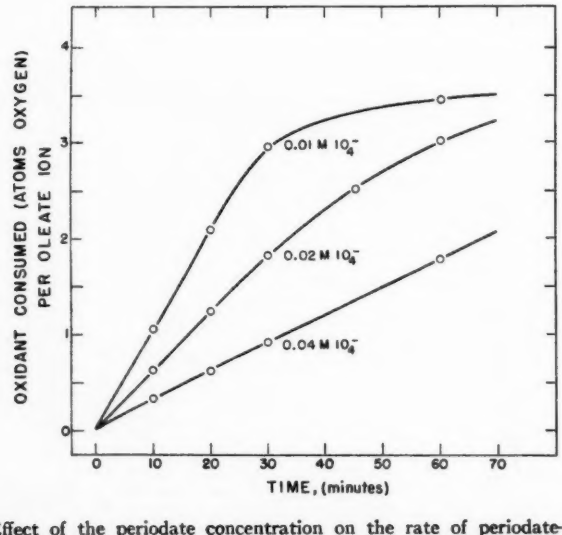

FIG. 6. Effect of the periodate concentration on the rate of periodate–permanganate oxidation of oleate using the conditions of Fig. 1, plot 1, except for the periodate concentration.

EXPERIMENTAL

Methods

The following procedure was used to follow the rates of oxidation. The required amounts of olefin and potassium carbonate were dissolved in water and the solution was made up to 100 ml. The periodate–permanganate reagent was made up freshly before use by mixing the required amounts of standard solutions of sodium *meta*-periodate and potassium permanganate and diluting to 100 ml. At zero time, 5-ml. volumes of the two solutions at the desired temperature were mixed in a glass-stoppered flask. The reaction was stopped by rapidly adding about 0.5 gm. sodium bicarbonate, a measured volume of standard arsenite solution, and a few crystals of potassium iodide. After this solution was left for at least 10 min., the excess arsenite was determined by slow titration of the stirred solution with standard iodine solution to the starch end point. The difference between the titers for a run and a reagent blank was taken as equivalent to the oxidant consumed. The pH values reported were measured soon after the reaction mixture was made up. In some experiments, potassium hydroxide was added to achieve the desired pH. The following procedure was used to determine the amounts of aldehyde and acid present in the reaction mixture (see Fig. 1). After a given reaction time, the oxidant was destroyed and the solution rendered strongly acid by the addition of an excess arsenite solution and 10% sulphuric acid. The resulting mixture was extracted continuously with ether. The extract was filtered and concentrated to a small volume. The acid content in the residue was determined by titration with standard methanolic sodium hydroxide to the phenolphthalein end point. The aldehyde content was determined by the hydroxylamine procedure of Siggia (13).

Runs with mixtures of heptanal, azelaic acid, and oleic acid showed the method reliable to within ±2% for the acid content and to within ±10% for the aldehyde content. Formaldehyde was determined colorimetrically using chromotropic acid (4, 7). The acetone liberated in the oxidation of mesityl oxide was removed from the oxidation mixture by distillation and determined by iodometric titration (9).

Oxidations of Oleic Acid

A reaction mixture, 400 ml., which contained initially 0.2824 gm. (1 mM.) of pure oleic acid, 3 mM. of potassium carbonate, 8 mM. sodium *meta*-periodate, and 0.134 mM. potassium permanganate was kept at 20°C. for 20 hr. The solution was rendered strongly acid by addition of 10% sulphuric acid and extracted with ether. The extraction yielded 0.354 gm. of material which on trituration with petroleum ether gave 161 mgm. of an oil with neutral equivalent 164. The oxidation would theoretically yield 0.158 gm. of pelargonic acid and 0.188 gm. of azelaic acid. The oil was distilled *in vacuo* and then gave a hydrazide of m.p. 93.5–94.5°C. (undepressed by pelargonic acid hydrazide m.p. 94–95°C. (8)). The residue from the trituration melted at 102–104.5°C. (undepressed by azelaic acid m.p. 106.5–107.5°C.) and was pure azelaic acid after recrystallization first from water and then from ethyl acetate.

A reaction mixture, 200 ml., was made up at 20°C. which contained 0.1412 gm. (0.5 mM.) oleic acid, 1.5 mM. potassium carbonate, 0.162 mM. potassium permanganate, and 0.2 mM. sodium *meta*-periodate. The initial pH was 7.7. Discoloration of the permanganate began in about three minutes and a large excess of sodium bisulphite was immediately added. The precipitate which formed on acidification was filtered off and triturated with cold petroleum ether to yield 35 mgm. of a substance, which was recrystallized from petroleum ether. The melting point, 60–62°C., of the material, 31 mgm., was not depressed by the mixture of ketohydroxystearic acids, m.p. 62–63.5°C., prepared by the method of King (3).

Almost exactly the same result was obtained when elaidic acid, m.p. 42.5–43.5°C., was oxidized under the above conditions except that the low solubility of the elaidate ion required that the reaction mixture be 2.5 times more dilute.

Oxidations of 10-Undecenoic Acid

10-Undecenoic acid was oxidized in the manner described above for oleic acid (Fig. 1, plot 1). Commercial undecenoic acid was distilled *in vacuo* to give a product of about 96% purity (iodine value 132); 0.190 gm. of the distilled acid yielded 0.192 gm. petroleum ether insoluble material, m.p. 126–131°C. Recrystallization from water and ethyl acetate yielded a product of m.p. 131–132.5°C. (undepressed by sebacic acid, m.p. 132–133°C.). The yield of formaldehyde was 73% (7).

The following procedure for preparing 10,11-dihydroxyundecanoic acid is similar to that described by Lapworth and Mottram (5) for the preparation of 9,10-*erythro*-dihydroxystearic acid. 10-Undecenoic acid, 0.68 gm., was dissolved with 1 gm. sodium hydroxide in 100 ml. of water and the solution was diluted to 800 ml. with ice-cold water. A 1% solution of potassium permanganate, 80 ml., was added with stirring. The mixture immediately changed in color to a dark green and was decolorized with sodium bisulphite after five minutes' reaction time. The solution was concentrated to 150 ml., made strongly acid with sulphuric acid, and extracted with ether. Evaporation of the dried ether extract to small volume led to the deposition of 0.50 gm. of a crystalline solid, m.p. 72–78°C. The material was recrystallized alternately from ethyl acetate and water to yield a substance, m.p. 67–69°C. Upon rapid recrystallization from acetone at −20 to −30°C. an acid was obtained, m.p. 83–84°C., which was undepressed in admixture with and possessed the same infrared spectrum as 10,11-dihydroxyundecanoic acid (m.p. 83–85°C.) prepared by the method of Swern *et al.* (14). The high and low melting forms could be readily interconverted by crystallization and both gave a *p*-bromophenacyl ester of m.p. 105–106°C. The material gave a negative 2,4-dinitrophenylhydrazine test, consumed oxidant equivalent to two atoms of oxygen on periodate–permanganate oxidation (as described above) with the formation of a mole of formaldehyde, and possessed the neutral equivalent (218) expected for 10,11-dihydroxyundecanoic acid (calc. 218.29).

10-Undecenoic acid (0.924 gm., 5 mM.) and potassium carbonate (5 mM.) were dissolved in 500 ml. of ice-cold water. An ice-cold solution of 5 mM.

potassium permanganate and 10 mM. sodium *meta*-periodate in 500 ml. water was added with stirring. After one minute, an excess of sodium bisulphite was added. The solution was concentrated to about 200 ml., cooled to about 2°C., and made strongly acid with cold 10% sulphuric acid. After the mixture had stood in the cold for 15 to 20 min., the precipitate was collected and dried, m.p. 83–89°C. Recrystallization from chloroform raised the melting point to 89–94°C. The following observations established the substance to be substantially pure 10-keto-11-hydroxyundecanoic acid. The infrared spectrum showed two bands in the carbonyl region and the material gave a positive 2,4-dinitrophenylhydrazine test. The material, neutral equivalent 220, liberated 1 mole of formaldehyde on periodate oxidation with the liberation, by titration, of 0.84 equivalent of acid per mole of periodate consumed. In a separate experiment, periodate oxidation gave a quantitative yield of crude sebacic acid, m.p. 119–129°C.; after two recrystallizations the compound had m.p. 130–132°C.

Oxidation of Ethylene

Ethylene, about 0.13 mM., was admitted to 200 ml. of solution containing 0.034 mM. potassium permanganate, 1.97 mM. sodium *meta*-periodate, and 0.25 mM. potassium carbonate kept in a nitrogen atmosphere. Highly erratic results were obtained when the reaction was performed in air. These results were probably due to the ability of permanganate to catalyze autoxidation (15). After it was shaken for 18 hr., the solution, pH 7.6, was analyzed as described above for oxidant content and for formaldehyde (7). Since the consumption of oxidant equivalent to 0.402 milliatoms of oxygen resulted in the formation of only 0.11 mM. formaldehyde, it is apparent that glycollic aldehyde is the first product of the reaction. It was established (7) that formaldehyde is oxidized only very slowly under these conditions.

ACKNOWLEDGMENTS

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PERIODATE–PERMANGANATE OXIDATIONS

II. DETERMINATION OF TERMINAL METHYLENE GROUPS[1]

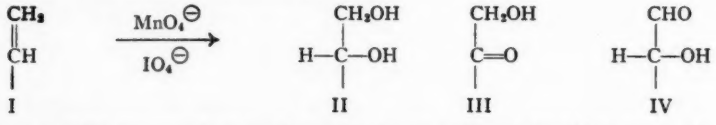
By R. U. Lemieux[2] and E. von Rudloff[3]

ABSTRACT

The periodate–permanganate oxidation of a terminal methylene ($CH_2{=}C<$) group can be made to produce formaldehyde in high although not quantitative yield. Since the yields compare favorably with those obtained by ozonolysis, the reagent can serve as the basis for a convenient micromethod for the estimation of terminal methylene groups. The less than theoretical yields of formaldehyde are believed mainly due to the conversion of the olefin in part to α-hydroxyaldehyde in the initial stage of the reaction.

INTRODUCTION

Results were reported in our first communication in this series (12) which indicated that the periodate–permanganate oxidation of a terminal methylene group (I) produces, simultaneously, in the first stage of the reaction, glycol (II), ketol (III), and hydroxyaldehyde (IV). Subsequent periodate oxidation of these substances produces formaldehyde from II and III but not from IV. Glycol formation did not appear extensive in weakly alkaline media since the oxidation of ethylene gave very nearly one mole of formaldehyde. However, oxidation of 10-undecenoic acid gave a 73% yield of formaldehyde (12). It was therefore evident that the ketol formation can be the preferred route and since the oxidant attacked formaldehyde only very slowly, it was apparent that the reagent deserved attention as a means for the semiquantitative estimation of terminal methylene groups.



We now wish to report on evidence that any attempt to obtain a maximum yield of formaldehyde in the periodate–permanganate oxidation of a terminal methylene group should consider: (*a*) the effect of pH on the reaction route, (*b*) the effect of pH on the rate of the periodate oxidation of glycols and acyloins, (*c*) the effect of pH on the rate of the permanganate oxidation of formaldehyde, and (*d*) the solubility of the compound in aqueous media.

Evidence has been obtained (12) that hydroxylation of the olefin is favored at a pH of 9–10 with acyloin formation predominating at a slightly lower pH. On this basis, it would appear desirable to operate at a high pH. However, the periodate–permanganate reagent does not operate above about pH 10 (12). Also, even at pH 10, the periodate oxidation of glycols is relatively slow (3, 14).

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[3]*National Research Council of Canada Postdoctorate Fellow, 1953–54.*

Furthermore, as seen in Fig. 1, formaldehyde is oxidized fairly rapidly at pH 10. Therefore, it is evident that should the pH of the media be maintained at a pH about 10, loss of formaldehyde would result from the oxidation of the formaldehyde and degradation of the glycol by the permanganate. Also, the use of alkaline media can be expected to give rise to formaldehyde from the enol

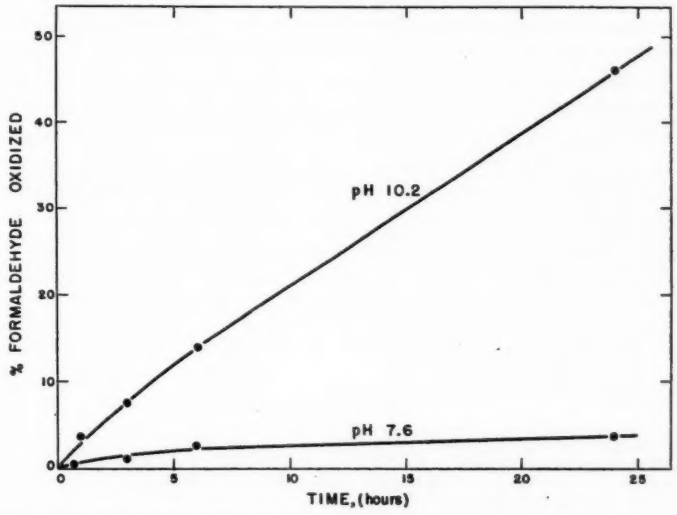

FIG. 1. Effect of pH on the rate of the oxidation of formaldehyde by the periodate–permanganate reagent.

form of methyl ketones thus complicating the results. On the other hand, the maintenance of the medium at near neutrality can be expected to result in the formation of appreciable amounts of hydroxyaldehyde. As a compromise to these conflicting effects, it was decided to carry out the oxidation for a short period of time at pH 10 and then to adjust the pH to near neutrality for completion of the reaction. The data listed in Table I show that this expedient gave in most cases a much improved yield of formaldehyde over that obtained when near neutral conditions were maintained throughout the reaction.

The yields of formaldehyde listed in Table I were determined colorimetrically using the chromotropic acid reagent according to the procedure of Lambert and Neish (10). The formaldehyde can also be determined by precipitation as the methone derivative (10, 13). In this case, larger samples are required and it is best to isolate the formaldehyde by distillation of the acidified reaction mixture before carrying out the precipitation. The present procedure should prove of value since it is easier to use than the standard methods of ozonolysis (4, 5), obviates the need of an expensive ozonizer, appears to provide higher yields of formaldehyde in many instances (see Table I), and may prove to be more reliable (6, 9, 15). The latter point is of importance since the detection of a terminal methylene group by infrared spectral analysis (2) must

TABLE I

TERMINAL METHYLENE GROUP ESTIMATIONS

(Maximum yields (per cent of theory) of formaldehyde obtained at pH∼7 and at pH∼10 with subsequent lowering to pH∼7)

Compound	Moles of CH_2O expected per mole of compound	pH∼7	pH∼10 → pH∼7	Reference
10-Undecenoic acid	1	73	97	
Itaconic acid	1	83	60	
Quinine	1	59	71	(9)[a]
Gelsemine	1	76	43	(8)
Isoatisine	1	76	50	(7)
Hydroxylactone	1	60	—	(1)[b]
Vinyl acetate	1	87	12(unstable)	(11)[c]
Allyl acetate	1	50	100(unstable)	
Allyl alcohol	2	57	—	
Allylamine	2	44	49	
Diallyl ether	2	55	89	
Allyl ethyl ether	1	56	81	
1-Allyl-2-thiourea	1	42	51	
Methacrylamide	1	45	69	(11)[c]
Acrylonitrile	1	14	50	
3-Butenenitrile	1	25	50	
3-Bromopropene	1	45	56	
Styrene	1	62	64	(4)[d]

[a]*Ozonolysis gave a 48% yield.*
[b]*Ozonolysis gave a 24% yield.*
[c]*Ozonolysis of a vinyl group and methyl methacrylate gave only 5% yields.*
[d]*Ozonolysis gave a 30% yield.*

be checked by chemical means. The method in its present form is restricted in scope by the fact that water is used as solvent. This limitation is not great, however, since only extremely low concentrations are required.

EXPERIMENTAL

The following procedures were used to determine the data listed in Table I and plotted in Fig. 1.

The compound, 0.005 mM., was dissolved in 5 ml. (or less) water contained in a 25 ml. volumetric flask. A quantity of 0.1 *N* potassium carbonate solution was then added to give the final solution a pH of 7 to 7.6. At zero time, 10 ml. of a solution of 0.02 *M* sodium *meta*-periodate and 1 ml. of 0.005 *M* potassium permanganate solution were added. The solution was made up to volume. Aliquots, 5 ml., were then transferred to 10 ml. volumetric flasks and after the desired time intervals, 15, 30, and 60 min., the reaction was stopped by the addition of 2 ml. of 1 *M* sodium arsenite solution and 2 ml. of 2 *N* sulphuric acid to a flask. The resulting solutions were then analyzed for their formaldehyde contents as described below, following the procedure of Lambert and Neish (10).

When it was desired to carry out the oxidation at higher pH's, 0.1 *N* potassium hydroxide was added to the solution before the addition of the oxidant. If it was desired to lower the pH back to near neutrality after a given period

of oxidation, an equivalent amount of hydrochloric acid was added before the solution was made up to volume. The data listed in Table I for pH about 10 with return to pH about 7 were obtained by adding 5 ml. of 0.1 *N* potassium hydroxide solution followed by 5 ml. of 0.1 *N* hydrochloric acid after about one minute's reaction time.

After the oxidation had been stopped, the solutions were allowed to stand for about 15 min., made up to volume (10 ml.), and 1-ml. aliquots were transferred to 25 × 200 mm. test tubes. Chromotropic acid reagent (1 gm. chromotropic acid in 100 ml. water, filtered and the filtrate made up to 500 ml. with 2:1 v/v concentrated sulphuric acid – water mixture), 10 ml., was added and the mixtures heated in a boiling water bath for 30 min. After the contents were cooled to room temperature, they were transferred to cuvettes for measurement of the per cent transmission at 570 mμ when compared to a reagent blank. Erythritol was used as standard for the production of known amounts of formaldehyde (2 moles of formaldehyde per mole of erythritol) in the setting up of a standard curve.

ACKNOWLEDGMENT

The authors are indebted to Dr. O. E. Edwards who supplied the alkaloids listed in Table I.

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PERIODATE–PERMANGANATE OXIDATIONS

III. DETERMINATION OF ISOPROPYLIDENE GROUPS[1]

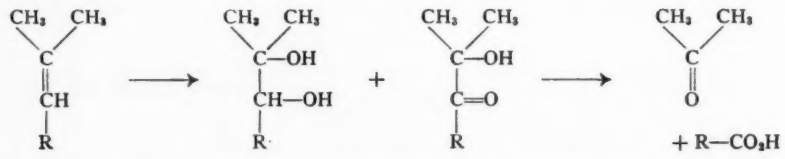
By E. von Rudloff

ABSTRACT

The reaction of the periodate–permanganate reagent with olefinic double bonds was applied to the determination of isopropylidene groups. The oxidation of compounds containing such groups gave a quantitative yield of acetone which could be readily determined by known iodometric and colorimetric procedures. Use of aqueous solutions of pyridine or dioxane as solvent permitted analysis of water-insoluble compounds. The colorimetric determination of acetone was then preferred. This method also allowed a simultaneous estimation of terminal methylene groups. The content of isopropylidene groups of commercial samples of three terpenes of the geraniol type was determined.

INTRODUCTION

The oxidation of olefinic double bonds with the periodate–permanganate reagent was described in part I of this series (2). From the general characteristics of this reaction the oxidation of an isopropylidene group would be expected to proceed as follows at pH 7–8:



each isopropylidene group yielding one molecule of acetone. At neutrality the acetone formed by the oxidation of mesityl oxide did not appear to react further with the reagent (2). The yield of acetone could, therefore, be used as a convenient measure of isopropylidene groups in general. In conjunction with the semiquantitative estimation of terminal methylene groups, described in part II (3), such a procedure should also make it possible to distinguish readily between these two positions of unsaturation, which would be of special interest in the study of terpenes and resin acids.

RESULTS AND DISCUSSION

In preliminary experiments the effect of pH on the stability of acetone in the oxidation mixture was determined. Table I shows the amount of oxidant consumed when acetone was oxidized at varying pH values with five times the amount of oxidant used in the standard procedure (2).

Since the hydroxylation and cleavage steps are relatively fast reactions (2), it is safe to assume that the amount of acetone lost owing to oxidation will be insignificant at a pH below 8.0.

Acetone can be conveniently determined both iodometrically (5) and colori-

[1]*Manuscript received August 9, 1955.*
Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Saskatchewan. Issued as Paper No. 204 on the Uses of Plant Products and as N.R.C. No. 3744.

TABLE I

OXIDANT CONSUMED BY ACETONE
Atoms oxygen/mole of acetone

	pH					
	5.4	6.6	6.9	7.3	7.7	8.0
After 70 hr.	0	0.03	0.04	0.05	0.10	0.40
After 142 hr.	0	0.06	0.07	0.10	0.19	0.78

metrically (7). In the former method the acetone was distilled from an alkaline solution after the excess oxidant had been destroyed with sodium arsenite solution. This method could not, however, be used when volatile compounds were present which react with iodine or alkaline iodine solution, unless these were removed by prior oxidation. The colorimetric method proved to be less accurate (the error was ±2%), but it had the advantage that aliquots could be used directly from the reduced reaction mixture. In addition, the color reaction is more specific and no interference was obtained when formaldehyde was present in concentrations more than twice that of acetone.

Water-soluble Compounds

From experiments using mesityl oxide as test substance the following conclusions were drawn:

(1) The amount of oxidant should be at least twice the theoretical amount required for complete oxidation as deduced from the above reaction scheme.

(2) Increasing the amount of permanganate in the periodate–permanganate reagent increases the rate of reaction (2), but too high a permanganate concentration results in a more rapid oxidation of the acetone formed.

(3) If other volatile compounds, such as aldehydes, are formed during the oxidation, these may be removed from the distillate by dichromate oxidation (4) in acidic medium at room temperature. Acetone itself is not oxidized under these conditions, but a second distillation step is then introduced into the procedure. As an alternative, the more convenient, though slightly less accurate, colorimetric determination of acetone may be used.

Under optimum conditions the yield of acetone was 95 to 96% of the theoretical. This represented a practically quantitative result, since the sample of mesityl oxide used gave after oxidation a yield of about 2% formaldehyde, indicating the presence of 2 to 3% of the isomer having the double bond in the 4,5-position. The presence of this isomer in mesityl oxide has been reported before (1).

Because of the possible interference with the iodometric determination by volatile reaction products or unreacted starting material from the oxidation of mesityl oxide, 3-methyl-2-butenoic acid appeared to be a more satisfactory test substance and was consequently prepared by hypochlorite oxidation of mesityl oxide (6). On oxidation this acid would be expected to yield acetone, oxalic acid, and carbonic acid, with glyoxylic acid and formic acid as intermediates. The only distillable product at any stage of the periodate–permanganate oxidation from an alkaline reaction mixture would therefore be acetone.

The rate of oxidation of 3-methyl-2-butenoic acid was similar to that of mesityl oxide, e.g. at pH 7 the amount of oxidant consumed was equivalent to 2.08, 3.09, 3.65, and 3.88 oxygen atoms after 0.05, 0.5, 3, and 70 hr. respectively. A formaldehyde determination indicated the presence of up to 2% of the Δ^3-isomer. The yield of acetone was determined iodometrically after different reaction times (from 5 to 360 min. at 5 to 10 min. intervals) with the reagent containing the normal and twice and four times the normal amount of potassium permanganate. A practically quantitative yield was obtained (98.8, 98.8, and 98.4 $\pm$0.4% respectively) within one hour of reaction time, and this yield did not appear to drop during a further period of two hours.

Water-insoluble Compounds

When the above procedure was applied to terpenes of the geraniol group, difficulty was encountered because of their insolubility. A study was therefore made of certain organic solvents which, when added to the aqueous reaction mixture, would increase the solubility sufficiently without interfering with the periodate–permanganate oxidation. Of the solvents tested only pyridine and dioxane proved suitable. Reagent blanks containing these solvents, especially dioxane, consumed appreciable amounts of iodine in excess of the aqueous reagent blank (Table II), but the oxidation of mesityl oxide appeared to be little altered in rate and degree by their presence (Table III). When pyridine

TABLE II

TITRATION OF REAGENT BLANKS CONTAINING 25% ORGANIC SOLVENTS TAKING COMPARATIVE AQUEOUS BLANKS AS 0
Ml. 0.025 *N* iodine solution

Medium	Time (hr.)				
	¼	½	1	3	24
25% Pyridine solution	0.10	0.15	0.22	0.36	0.72
25% Dioxane solution	1.34	1.36	1.39	1.54	3.58

TABLE III

OXIDANT CONSUMED (ATOMS OXYGEN/MOLE) BY MESITYL OXIDE IN VARIOUS MEDIA UNDER STANDARD CONDITIONS

Medium	pH	Time (hr.)							
		1/12	⅛	⅓	1	3	22	46	72
Aqueous	7.2	3.0	3.05	3.20	3.50	3.75	3.97	4.00	4.04
Aqueous	7.7	3.05	—	3.28	3.56	3.82	3.98	4.02	4.06
25% Pyridine	8.4	3.12	—	3.24	—	3.48	3.90	4.05	4.11
25% Dioxane	7.3	2.94	3.22	3.44	—	3.84	—	—	—

was used the pH of the reaction mixture was 8.4 and the addition of potassium carbonate was therefore omitted. The reaction mixture containing 25% dioxane decolorized overnight and the reaction stopped. This may have been due to the regeneration of permanganate by periodate being slowed down to a critical value. When 30% or more solvent was used, this phenomenon was

noticed at an earlier stage. However, the early part of the reaction involving the formation of acetone is relatively fast and a quantitative yield of acetone could still be obtained.

Difficulties were experienced when the iodometric method for determining acetone was used since most of the solvent distilled over with the acetone. With dioxane the error introduced was not large, but when pyridine was used the procedure had to be modified by introducing a second distillation step. After the acetone and pyridine from the first distillation was collected, excess 10% sulphuric acid (20–25 ml.) was added and the acetone was redistilled. Although the results obtained by this modification were satisfactory, the procedure was cumbersome and the colorimetric method was preferred. The latter method gave results similar to those with aqueous solutions as long as the reagent blank and reference samples contained the same amount of solvent.

3-Methyl-2-butenoic acid was oxidized in the different solvent systems under the usual conditions, and aliquots were analyzed colorimetrically after various reaction times. The time required to reach a maximum yield of acetone was different for each medium, but the maximum values were maintained for 5 to 10 min. After this period the yield dropped somewhat faster than would be expected from the rate of oxidation of the acetone (in an aqueous medium) alone. The results obtained were:

(1) in aqueous solution = 99% of theoretical (maximum after 10 min.),
(2) solution containing 25% pyridine = 100% (maximum after 30 min.),
(3) solution containing 25% dioxane = 99% (maximum after 20 min.).

The foregoing results show that the procedures outlined should be of value in both structure determination and routine analysis, especially since as little as 0.01 mM. of a substance was sufficient for quantitative results. The use of the reagent for determining the position of double bonds in unsaturated fatty acids and related compounds will be the subject of a future communication.

Application to Terpenes

The method was applied to the analysis of three commercial samples of terpenes. Each compound gave the maximum yield of acetone (see Table IV)

TABLE IV

YIELDS OF ACETONE* FROM TERPENES
Per cent of the theoretical

Medium	Terpene		
	Geraniol	Citronellol	Citronellal
Solution containing 25% pyridine	88	79	77
Solution containing 30% dioxane	89	81	79

Colorimetric procedure.

already after 5 to 10 min. These results show that in each of the terpenes the isomer having the isopropylidene grouping is the major component. The same

reaction mixtures were also analyzed for their content of formaldehyde resulting from the presence of terminal methylene groups. The maximum yields for geraniol, citronellol, and citronellal were 43%, 4%, and 8.5% respectively.

EXPERIMENTAL

Apparatus

The condenser was constructed of capillary glass-tubing surrounded by an ordinary cooling jacket. The tubing extended into the receiver so that the distillate was collected under 10 to 15 ml. of water. The receiver was surrounded by ice water. The connection to the distillation flask was through a standard glass joint.

The colorimetric measurements were carried out with a Coleman electrophotometer (Junior 6A).

Reagents

Analytical grade reagents and solvents were used. Mesityl oxide (Eastman Kodak) was redistilled through a Podbielniak fractionating column. Pyridine and dioxane were further purified by treating with weak alkaline permanganate solution for 16 hr. at room temperature and redistilling over solid potassium hydroxide after the excess permanganate had been reduced.

3-Methyl-2-butenoic acid was synthesized by hypochlorite oxidation of mesityl oxide (6) and was purified by recrystallization from water and light petroleum, m.p. 67–68°C. (reported m.p. 66–67.5°C.); neutralization equivalent found 100.7, calc. 100.1. The terpenes were of technical or practical grade (Eastman Kodak) and were not purified further.

Periodate–Permanganate Oxidant

The stock solution of the oxidant contained 20.980 gm. (98.33 mM.) sodium *meta*-periodate and 167 ml. 0.01 *M* (1.67 mM.) potassium permanganate per liter. In experiments using two or four times the concentration of permanganate, the amount of periodate was reduced in order to maintain the total concentration of oxidant at 100 mM. per liter.

Standard Procedure of Oxidation

The substance to be oxidized, 0.5 mM., was dissolved in distilled water, or where necessary, in the required amount of organic solvent, and the solution was made up to 100 ml. with distilled water. To 50 ml. of this solution sufficient potassium carbonate was added (about 25 mgm. for a neutral substance) to give the final reaction mixture a pH of 7.2 to 7.5. To this solution 20 ml. stock oxidant solution was added with shaking, the time of addition being noted, and the solution was quickly made up to 100 ml. Aliquots of 10 ml. were analyzed at the desired time intervals by the method described in part I (2).

Periodate–Permanganate Oxidation and Iodometric Acetone Determination

Aliquots of 10 ml. of the oxidation mixture were placed in 100 ml. flasks having ground glass joints. At the required time interval the oxidation was stopped by adding to each aliquot 1 ml. 1 *M* sodium arsenite, 1 ml. 2 *N* NaOH, and 10 to 15 ml. water. About half the volume of this solution was distilled,

the distillate being collected in 10 to 15 ml. ice-cooled water. Five milliliters 2 *N* sodium hydroxide and 5.0 ml. 0.1 *N* iodine solution were added to the distillate and this solution was allowed to stand out of contact with direct sunlight for 10 to 15 min. Five milliliters 10% sulphuric acid was then added and the liberated iodine was titrated with 0.025 *N* sodium thiosulphate to the starch end point. When dioxane was present 10–15 ml. sulphuric acid had to be added. When pyridine was present the distillate was treated with excess 10% sulphuric acid (approx. 20 ml.) and redistilled. In this way the iodometric determination could be carried out without interference from the pyridine.

Periodate–Permanganate Oxidation and Colorimetric Acetone Determination

The solution of the compound to be oxidized, 2.0 ml., was pipetted into a 25 ml. volumetric flask and 2.0 ml. 0.1 *N* potassium carbonate, 10 ml. water, and 8.0 ml. stock oxidant solution were added. The solution was made up to 25 ml. after noting the time when the oxidant was added. Aliquots of 5.0 ml. of this reaction mixture were pipetted into 10 ml. volumetric flasks and after 5, 10, 20, or 30 min. reaction time 2.0 ml. 1 *M* sodium arsenite and 2.0 ml. 2 *N* sulphuric acid were added. The solutions were allowed to stand for 15 to 30 min., when 0.4 ml. 10 *N* sodium hydroxide (enough to neutralize the solution) was added to each sample, and these were then made up to 10 ml. These solutions could be kept for several hours before colorimetric analysis. Aliquots of 2.0 ml. of each sample were pipetted into a 25 × 200 mm. test tube and 3.0 ml. distilled water was added. When all samples, reagent blanks, and reference standards were thus prepared, 4.0 ml. 10 *N* sodium hydroxide was added with a syringe and finally, with mixing, 1.0 ml. of salicylic aldehyde solution. The salicylic aldehyde solution (1 volume of the aldehyde and 4 volumes ethanol) was used within five to six hours after preparation. The test tubes were immediately placed in a water-bath at 50°C., kept at 45–50°C. for 20 min. and then at room temperature for 30 min. The contents were transferred to 19 mm. cuvettes for immediate measurement of the percentage transmission at 530 mμ as compared to a reagent blank.

Formaldehyde Determinations

Aliquots of 1.0 ml. from the reaction mixture in the 10 ml. volumetric flasks could be used directly and these were analyzed as described in part II (3).

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OZONOLYSIS OF 1-SUBSTITUTED CYCLOOLEFINS[1]

By D. G. M. Diaper[2]

ABSTRACT

Extension of an aliphatic chain by five, six, or seven carbon atoms may be achieved by adding to it a 5-, 6-, or 7-membered olefinic alicycle and subsequently breaking the double bond. Addition of the ring is achieved by a Grignard reaction between an alkylmagnesium bromide and a cyclic ketone, and the resulting 1-alkylcycloolefin is opened by ozonolysis. The end product is a 5-, 6-, or 7-keto acid.

Methods for extension of the aliphatic chain fall into two main groups; those in which one or two carbon atoms are added, and those in which the starting material and added fragment are of comparable chain length. To the former class belong the familiar cyanide and malonic ester syntheses. These are regarded as inferior in long-chain work because end products and starting materials have similar chain-lengths (and thus similar physical properties) and are difficult to separate from each other. Methods of the latter class include the Robinson (5), Noller and Adams (4), and Blaise (1) syntheses, in which a large increment is added in one step and end product is easily separated from relatively short-chain starting materials. These methods suffer from the limited accessibility of such necessary chain-extending reagents as ω-bromo, -cyano, or -aldehydo esters or ω-carbalkoxy acid halides.

Extension using an alicyclic fragment which is subsequently opened to become part of the chain is a tempting approach. Fieser and Smuszkovicz (2) showed that 1-substituted cycloalkanols (from cycloalkanones and a Grignard reagent) may be oxidized to keto acids by chromic acid at 30° in the presence of large amounts of anhydrous acetic acid. Kelkar, Phalnikar, and Bhide (3) encountered difficulty in an attempt to make a keto acid from a 1-alkylcyclohexene by strong oxidation. Schneider and Spielman (7) concluded that chromic acid oxidation of a 1-alkylcyclohexene was inferior to the alkylzinc synthesis of a keto acid. In all investigations there was evidence of concurrent reactions. If linkages other than those intended are attacked, as may well happen when oxidizing agents of poor selectivity are employed, the same problem of separation of end product from lower homologues may be encountered.

In the present investigation, opening of the alicyclic system was achieved by ozonolysis and the resulting keto aldehydes were oxidized by performic acid to the corresponding keto acids. These are "clean" reagents of high specificity and the end products in all cases were nearly white and reasonably pure. A prerequisite for success of the synthesis is unambiguity of location of the olefinic linkage. Wallach (10) has shown that, in general, dehydration of a 1-alkylcyclohexanol gives the olefin with the cyclic rather than the semicyclic double bond. During ozonolysis of the olefins of this investigation, no evidence of alkylidenecycloalkanes was encountered.

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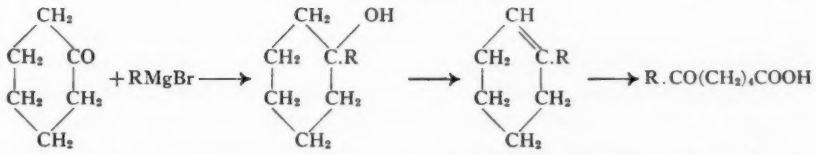
Contribution from the Department of Chemistry, Royal Military College, Kingston, Ontario.
[2]*Department of Chemistry, Royal Military College.*



The use of cyclohexanone is illustrated above in the extension of a chain by six carbon atoms giving a 6-keto acid. It is also found that a 5-keto acid may be obtained from cyclopentanone and a 7-keto acid from cycloheptanone. Yields in the two-step synthesis are indicated in Tables I and II.

TABLE I

OLEFINS

Name	Yield, %*	B.p., °C./mm.	n_D^{20}	C and H, %			
				Calc.		Found	
				C	H	C	H
1-*n*-Butylcyclopentene	56	51–53/18	1.4478				
1-*n*-Butylcyclohexene	40	71–73/18	1.4592				
1-*n*-Amylcyclopentene	52	176–177/760	1.4540				
1-*n*-Butylcycloheptene	40	87–92/19	1.4695†	86.8	13.2	86.7	13.2
dl-1-(2-Methylbutyl)cyclohexene	25	193–194/760	1.4600	86.8	13.2	86.6	12.9
1-Phenylcyclohexene	62	122–125/11	1.5669†				
1-*n*-Hexylcyclohexene	43	104–109/19	1.4560	86.7	13.3	86.6	13.0
1-*n*-Octylcyclohexene	36	121–127/12	1.4683				
1-(10-Undecenyl)cyclopentene	28	139–151/13	1.4908	87.3	12.7	87.1	13.0

*Based on cyclic ketone.
†25°.

TABLE II

KETO ACIDS

Name	Yield, %	M.p., °C.	Acid equivalent		Semicarbazone		
			Calc.	Found	M.p., °C.	N analysis, %	
						Calc.	Found
5-Ketononanoic acid	43	44			132–133	18.3	18.2
6-Ketodecanoic acid	61–68	46–47			160	17.3	17.2
5-Ketodecanoic acid	67–73	57			111	17.3	17.1
7-Ketoundecanoic acid	63	51.5–52	200	202	133	16.3	16.3
6-Keto-8-methyldecanoic acid	76	33–34	200	204	120	16.3	15.9
5-Benzoylpentanoic acid	69	78			182–183		
6-Ketododecanoic acid	71	62.5–63	214	216	130–131	15.4	15.5
6-Ketotetradecanoic acid	60	66	242	246	120–121	14.0	14.0
4-Ketotridecane-1,13-dicarboxylic acid	27	108	286	286	130		

Losses in the synthesis of 1-alkylcycloolefins are attributable (cf. 6, 8) to two main causes, "coupling" of the Grignard reagent giving a paraffin hydrocarbon and reduction of the cyclic ketone giving an olefin and cycloalkanol. "Coupling" appears to be more serious when higher alkyl halides are employed, and reduction appears to be favored by branching of the Grignard reagent and by increase in the size of the alicycle. It was found to be least in the reaction involving phenylmagnesium bromide.

EXPERIMENTAL

Synthesis of 1-Substituted Cycloolefins

The procedure outlined below in the synthesis of 1-*n*-butylcyclohexene from cyclohexanone and *n*-butylmagnesium bromide is typical for all olefins listed in Table I (cf. Signaigo and Cramer (8)). Cyclohexanone (47 gm., 0.48 mole) was added during eight and one-half hours to the Grignard reagent from *n*-butyl bromide (71 gm., 0.52 mole) and magnesium (12 gm., 0.50 mole) in 200 cc. of dry ether, cooled with solid carbon dioxide to maintain an internal temperature of −40 to −20°C. Next day, the mixture was added to ice and hydrochloric acid in excess, and the ethereal solution was washed with water, three times with a saturated aqueous solution of sodium bisulphite (to remove cyclohexanone), and with potassium carbonate solution before it was dried over sodium sulphate. The product, a tertiary alcohol, was not purified, but used directly in the next stage.

Dehydration of 1-*n*-butylcyclohexanol was achieved by heating with iodine (0.2 gm., cf. 11) at reflux in an apparatus provided with a water separator. The theoretical quantity of water was collected in one and one-half hours, and the liquid remaining was fractionally distilled through a 15 cm. Widmer column. To avoid overheating during dehydration of higher tertiary alcohols it was found desirable to add xylene as a diluent. 1-*n*-Butylcyclohexene (26 gm., 40%) boiled at 71–73° at 17 mm. and had n_D^{20} 1.4592. On standing in air, the liquid darkened somewhat, became more viscous, and had a higher refractive index. This was taken to indicate polymerization, and the olefin was utilized as soon as possible in the next step.

Oxidation of 1-Substituted Cycloolefins to Keto Acids

The general procedure employed is described here for the case in which 1-*n*-butylcyclohexene was converted, by ozonolysis, to 6-ketodecanal, and this aldehyde was oxidized to the corresponding acid by performic acid, generated *in situ*. A slow stream of oxygen containing approximately 6% of ozone was passed into 1-*n*-butylcyclohexene (20 gm., 0.15 mole) in acetic acid (20 cc.) until a test sample failed to decolorize bromine and for 10 min. afterward. A technique similar to that of Noller and Adams (4) was used to decompose the ozonide as follows: The viscous solution was diluted with an equal volume of ether, cooled in ice, and treated cautiously with several cubic centimeters of water and 1 gm. (0.01 mole) of zinc dust. There ensued a violent reaction after an induction period, and next day the solution was filtered and separated. The ether solution was washed with water, and then 20 cc. of hydrogen peroxide (30%, 0.2 mole), 25 cc. of formic acid (90%), and 1 gm. of ammonium acetate were added. After 24 hr. at room temperature the mixture was diluted with ether and water and separated. The ethereal layer was shaken with several portions of aqueous ferrous sulphate until free from peroxides, and the acidic product was freed from neutral impurities using potassium carbonate solution in the usual manner. After removal of ether, 6-ketodecanoic acid was recrystallized from petroleum ether; the yield was 61–68% in several runs and the acid melted at 46–47°.

A simplification of the oxidation procedure was made possible by the obser-

vations that formic acid may replace acetic acid as an ozonization solvent and that performic acid oxidation appears to be unaffected by the presence of zinc salts. In the modified procedure, 21 gm. of 1-*n*-butylcyclohexene in an equal volume of formic acid was treated with ozonized oxygen as before except that care was necessary in using the bromine test as the formic acid gradually decolorized bromine. After treatment with zinc, water, and ether, the reaction mixture was filtered but not washed before treatment with a further 20-cc. portion of formic acid and 20 cc. of 30% hydrogen peroxide. The yield of keto acid was 16.5 gm. (58%).

A neutral fraction was obtained in varying quantity after performic acid oxidation of 6-ketodecanal. It was shown to contain unchanged aldehyde, as a second treatment with performic acid gave some 6-ketodecanoic acid. There remained, however, a residual neutral fraction, corresponding to 10–15% of the starting material, which was not an aldehyde and showed evidence of unsaturation. This material will be further studied.

Ozonolysis of 1-Phenylcyclohexene

A modified procedure was employed in the ozonolysis of the aromatic hydrocarbon 1-phenylcyclohexene. By a technique similar to that of Dawson (9) this substance was ozonized in ethyl acetate at −70° under conditions designed to avoid over-ozonization with attack of the benzene nucleus. Following catalytic hydrogenation of the ozonide, the ethyl acetate solution containing 5-benzoylpentanal was treated with performic acid as previously described. From 11.4 gm. of starting material, the yield of 5-benzoylpentanoic acid was 10.3 gm. (69%), melting at 75°.

Undecenyl Bromide

1-Bromoundec-10-ene (undecenyl bromide) made by the action of phosphorus tribromide upon the corresponding alcohol must be freed from unchanged alcohol before use in the Grignard reaction. This cannot be achieved by distillation, as the two compounds have similar boiling points. The crude bromide (80 gm.) was taken up in dry ether (150 cc.) and treated with 20 gm. of phosphorus pentoxide. Next day, a further 20-gm. portion of phosphorus pentoxide was added, and the mixture was frequently shaken during the next four hours and then decanted into 250 cc. of 50% aqueous methanol. Concentrated aqueous ammonia was quickly added until the mixture was alkaline to phenolphthalein, and after it was washed with a similar portion of aqueous-methanolic ammonia and with water, the ether solution was dried and distilled.

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NOUVELLES SYNTHÈSES DE L'ACIDE GLUTARIQUE, DE LA GLUTARIMIDE ET DE L'ACIDE GLUTAMIQUE

PRÉPARATION DE LA N-BROMOGLUTARIMIDE[1]

PAR GÉRARD PARIS, ROGER GAUDRY ET LOUIS BERLINGUET

RÉSUMÉ

La monoamide de l'acide glutarique a été obtenue par condensation du cyanure de potassium avec la γ-butyrolactone, suivie de neutralisation et d'hydrolyse partielle du sel de potassium du nitrile intermédiaire. Cette monoamide a été facilement hydrolysée pour donner quantitativement l'acide glutarique. La glutarimide a été obtenue avec un excellent rendement, en cyclisant par chauffage, la monoamide de l'acide glutarique. L'ester éthylique monobromé de l'acide glutarique, préparé à partir de l'acide glutarique, a été condensé avec la phtalimide de potassium par chauffage dans la diméthylformamide. L'hydrolyse de ce dérivé phtalimidé a donné l'acide glutamique avec un bon rendement. La N-bromoglutarimide a été préparée à partir de la glutarimide par bromuration en présence d'hydroxyde de potassium. Cette N-bromoglutarimide s'est comportée, dans les quelques essais effectués à date, comme un bon agent de bromuration, comparable à la N-bromosuccinimide.

Les synthèses de l'acide glutarique et de la glutarimide sont assez nombreuses. On s'est servi comme produits de départ de l'acide L-glutamique naturel (6), du dicyanure de triméthylène (16, 21), de la cyclopentanone (14), de la δ-hydroxyvaléraldéhyde (3) de l'acrylonitrile et des esters β-cétomaloniques (17), du dihydropyranne (8), et enfin de la pipéridine (27).

Les produits de départ des principales synthèses de l'acide glutamique sont aussi nombreux: acide lévulique (25), acide β-aldéhydopropionique (12), acide α-cétoglutarique (13, 15, 24), ester acylaminomalonique (7, 9, 22).

Toutefois peu de ces synthèses sont pratiques, soit à cause des faibles rendements, soit à cause de la rareté relative des produits de départ.

Récemment Pichat, Baret et Audinot (18) ont montré que la β-méthylbutyrolactone s'ouvrait facilement en présence de cyanure de potassium à une température de 280°C. pour donner le sel de potassium du mononitrile correspondant. Ce sel de potassium leur a permis d'obtenir avec d'excellents rendements l'acide β-méthylglutarique et la β-méthylglutarimide.

Dans le but d'élaborer une synthèse simple et facile de l'acide glutarique et de la glutarimide, nous avons repris cette synthèse et l'avons appliquée à la γ-butyrolactone, produit facilement accessible.

La γ-butyrolactone a été condensée avec le cyanure de potassium à 190°C. Le sel de potassium du mononitrile formé n'a pas été isolé mais immédiatement neutralisé par l'acide chlorhydrique concentré, soit à une température de 25°C. pour donner la monoamide de l'acide glutarique avec un rendement de 80%, soit à 0°C. pour donner le mononitrile de l'acide glutarique avec un rendement de 65%. Par hydrolyse de ces deux derniers produits, l'acide glutarique a été obtenu avec un rendement quantitatif dans le cas de la monoamide et un rendement de 80% dans le cas du mononitrile.

[1]*Manuscrit reçu le 25 juillet, 1955.*
Contribution du Département de Biochimie, Faculté de Médecine, Université Laval, Québec, Québec.

La glutarimide est formée avec un rendement de 84% par cyclisation de la monoamide de l'acide glutarique à une température de 210°C.

Cette synthèse permettait de préparer facilement et avec d'excellents rendements l'acide glutarique et la glutarimide. Ces deux produits intermédiaires ont été utilisés pour de nouvelles synthèses de l'acide glutamique et de la N-bromoglutarimide.

Dans une nouvelle synthèse de l'acide glutamique, nous avons d'abord préparé le diester éthylique monobromé de l'acide glutarique suivant la méthode décrite par Ingold (11). Ce diester fut condensé avec la phtalimide de potassium. Le produit de condensation fut hydrolysé pour donner l'acide glutamique avec un rendement total de 50%, calculé à partir de l'acide glutarique.

La N-bromoglutarimide a été préparée à partir de la glutarimide suivant une méthode de synthèse identique à celle de la N-bromosuccinimide. Le rendement brut en N-bromoglutarimide est de 62%.

La N-bromoglutarimide ainsi préparée semble se comporter dans les essais effectués à date comme un bon agent de bromuration. C'est ainsi que nous avons bromé l'acétanilide, la triéthylamine. Nous avons oxydé l'alanine et finalement, nous avons effectué la bromuration allylique du méthylcrotonate. Les rendements obtenus se comparent avantageusement avec ceux décrits pour la N-bromosuccinimide.

PARTIE EXPÉRIMENTALE

Monoamide de l'acide glutarique

On ajoute du cyanure de potassium (17 g., 0.26 mole) à de la γ-butyrolactone (20.9 g., 0.24 mole) et on agite mécaniquement. On élève rapidement la température du mélange et on la maintient à 190°C. pendant trois heures après quoi on refroidit la solution. Le solide formé est repris à l'eau (50 ml.) et neutralisé avec un équivalent d'acide chlorhydrique (ou d'acide sulfurique concentré) à une température de 25°C. On ajoute un léger excès d'acide chlorhydrique (19.5 ml. en tout) et on laisse reposer quelque temps. On extrait la monoamide à l'éther. L'éther est séché sur du sulfate de sodium anhydre, puis évaporé à sec sous pression réduite. L'huile résiduelle brunâtre pèse 25.5 g. Rendement brut: 80%.

Par distillation fractionnée de cette huile, on obtient la monoamide contaminée par un peu de la glutarimide formée par chauffage lors de la distillation, lequel mélange distille à 150–155°C. sous 4.5 mm. La monoamide pure est extraite à l'éther. Point de solidification 14–15°C., $n_{20} = 1.450$. Calculé pour $C_5H_9O_3N$: N, 10.69%. Trouvé: N, 10.60%.

Acide glutarique

(*a*) *À partir de la monoamide*

On dissout la monoamide brute (5 g., 0.038 mole) dans 50 ml. d'eau et on ajoute 50 ml. d'acide chlorhydrique concentré. Le mélange est chauffé à reflux pendant une heure. On évapore la solution à sec sous pression réduite. On dissout le résidu dans l'eau chaude et on le décolore au noir animal. L'eau

est évaporée sous pression réduite. Par recristallisation du chloroforme bouillant, on obtient l'acide glutarique, débarrassé du chlorure d'ammonium insoluble. Le rendement est quantitatif: 5.02 g. P. f. 98–99°C. Litt: 97.5°C. (16).

(*b*) *À partir du mononitrile*

Le mononitrile (5 g., 0.04 mole) est hydrolysé de la même façon sauf que la durée de l'hydrolyse est portée de une à trois heures. Rendement: 4.67 g., 80%. P. f. 98–99°C. Litt: 97.5°C. (16).

Mononitrile de l'acide glutarique

La neutralisation lente à 0°C. avec un équivalent d'acide chlorhydrique concentré (19 ml.) du produit de condensation obtenu en traitant la γ-butyrolactone (16.5 g., 0.19 mole) par le cyanure de potassium (13 g., 0.20 mole) donne le mononitrile correspondant. On extrait le nitrile à l'éther lequel est séché sur du sulfate de sodium anhydre, puis évaporé à sec sous pression réduite. Le nitrile ainsi obtenu est recristallisé d'un petit volume d'éther pour enlever les traces de monoamide présente laquelle est beaucoup plus soluble. Rendement: 14.1 g., 65% P. f. 41–42°C. Litt: 45°C. (5). Calculé pour $C_5H_7O_2N$: N, 12.39%. Trouvé: N, 12.42%.

Glutarimide

(*a*) *À partir de la monoamide*

Dans un ballon de 50 ml. à un col surmonté d'un réfrigérant à air, on place la monoamide brute (5 g., 0.04 mole). On élève rapidement la température et on la maintient à 210–215°C. pendant trois heures. La solution est refroidie, après quoi on dissout le résidu dans l'eau chaude et on le décolore au noir animal. L'eau est évaporée sous pression réduite. Le résidu est recristallisé de l'alcool éthylique. Rendement 3.6 g., 84%. P. f. 154°C. Litt: 154.5°C. (27). Calculé pour $C_5H_7O_2N$: N, 12.38%. Trouvé: N, 12.39%.

(*b*) *À partir de l'acide glutarique*

Le chauffage de l'acide glutarique en présence d'ammoniaque concentré suivant la méthode habituelle (1) donne la glutarimide avec un bon rendement quoique le rendement total, calculé à partir de la γ-butyrolactone, soit inférieur à celui obtenu en passant par la monoamide.

Diester éthylique de l'acide 2-bromoglutarique

Le diester éthylique de l'acide 2-bromoglutarique est préparé à partir de l'acide glutarique par traitement au chlorure de thionyle, bromuration et réaction avec l'alcool éthylique, suivant la méthode décrite par Ingold (11). Le rendement a toutefois été augmenté de 50% à 80–85% en effectuant la bromuration avec l'aide de rayons ultraviolets.

Acide glutamique

Dans un ballon à trois cols, muni d'un agitateur et d'un réfrigérant surmonté d'un tube de chlorure de calcium, on ajoute de la phtalimide de potassium (18 g., 0.097 mole) à un mélange du diester éthylique de l'acide 2-bromoglutarique (25 g., 0.094 mole) et de 100 ml. de diméthylformamide. On agite une heure à la température d'ébullition de la diméthylformamide (152–154°C.).

La solution est refroidie. On filtre le précipité de bromure de potassium (9.5 g., théorie 11.1 g.). On évapore la solution à sec sous pression réduite et on ajoute de l'acide chlorhydrique concentré. On chauffe à reflux pendant 15 h. puis on évapore à sec. On reprend à l'eau et, après refroidissement, on filtre l'acide phtalique (15.5 g., théorie 16.1 g.) La solution est concentrée à faible volume, amenée à un pH de 3.2 au moyen de NaOH 10%, et placée à la glacière pendant plusieurs heures. Une première fraction (8.5 g.) précipite. Au bout de plusieurs jours on obtient une seconde fraction (2 g.). Rendement brut en acide glutamique: 10.5 g., 76%. Après recristallisation de l'acide aminé de l'alcool et de l'eau le p. f. est de 180–185°C. Litt.: 198°C. (26). Calculé pour $C_5H_9O_4N$: N, 9.52%. Trouvé: N, 9.48%. L'acide glutamique fut identifié par chromatographie sur papier ascendante et circulaire avec la pyridine à 80% comme solvant: R_f 0.21. De plus l'acide glutamique, étant un acide aminé monoaminé dicarboxylique, a été analysé par électrophorèse sur papier (pH 8.6, 4 ma., 200 volts). La bande obtenue après révélation à la ninhydrine correspondait exactement avec celles d'échantillons commerciaux d'acide glutamique.

L'acide glutamique fut aussi préparé à partir du diester éthylique monobromé de l'acide glutarique en présence d'ammoniaque sous pression. La présence de sels d'ammonium interfère toutefois dans l'isolement de l'acide libre.

N-Bromoglutarimide

On ajoute avec agitation rapide de la glutarimide (5 g., 0.044 mole) à une solution d'hydroxyde de potassium (2.78 g. de KOH dans 10 cc. d'eau) maintenue à −5°C. Au bout d'une minute, on ajoute rapidement et en une seule addition 7.1 g. de brome. Le solide formé (5.3 g., 62%) est filtré, lavé à l'eau froide, et recristallisé immédiatement de l'eau chaude. Rendement de la N-bromoglutarimide: 4.4 g., 52%; p.f. 185–190°C. d. Calculé pour $C_5H_6O_2NBr$: C, 31.40%; H, 3.14%; N, 7.13%; Br, 41.62%. Trouvé: C, 28.60%; H, 3.02%; N, 6.30%; Br, 44.08%. On peut aussi recristalliser la N-bromoglutarimide de l'acide acétique glacial.

Lorsqu'on solubilise la glutarimide dans une solution d'hydroxyde de potassium au lieu d'une solution d'hydroxyde de sodium, la N-bromoglutarimide obtenue est plus pure et plus facile à recristalliser, quoique les rendements obtenus lors de la bromuration soient inférieurs.

Réactions effectuées à l'aide de la N-bromoglutarimide

(*a*) *p-Bromoacétanilide*

La méthode est identique à celle décrite par Buu-Hoi' (4) pour la N-bromosuccinimide. Le résidu obtenu est recristallisé d'un mélange d'alcool et d'eau. Le rendement en *p*-bromoacétanilide est quantitatif. P. f. 167°C. Litt: 167°C. (10). Calculé pour C_8H_8ONBr: N, 6.5%; Br, 37.4%. Trouvé: N, 6.5%; Br, 37.5%.

(*b*) *Bromhydrate de la triéthylamine*

La méthode est la même que celle décrite par Braude et Waight (2) pour la N-bromosuccinimide. On ajoute en faibles portions de la N-bromoglutarimide à une solution de triéthylamine dans du tétrachlorure de carbone

refroidie à 0°C. Le solvant est évaporé. La glutarimide est extraite à l'acétone. Le bromhydrate fond à 245°C. Litt: 245–246°C. (2).

(*c*) *Dérivé 2,4-dinitrophénylhydrazone de l'acétaldéhyde, obtenu à partir de l'alanine*

La méthode est la même que celle décrite par Schönberg et collaborateurs (23) pour la N-bromosuccinimide. On ajoute de la N-bromoglutarimide à une solution aqueuse d'alanine. Après 10 min., on refroidit la solution et on ajoute du chlorhydrate de la 2,4-dinitrophenylhydrazine. Après recristallisation de l'alcool le dérivé fond à 146°C. Litt: 147°C. (19).

(*d*) *γ-Bromométhylcrotonate*

La méthode est la même que celle décrite par Ziegler et collaborateurs (28) pour la N-bromosuccinimide. On ajoute de la N-bromoglutarimide à un grand excès de méthylcrotonate et on chauffe à reflux pendant une heure. La solution est ensuite refroidie et la glutarimide formée est filtrée. Le γ-bromométhylcrotonate distille à 65°–68°C. sous 4.5 mm. $n_{20} = 1.495$. Litt: $n_{19} = 1.498$ (20).

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NOTES

A QUARTZ SPIRAL-TORSION MICROBALANCE*

By W. Bushuk† and C. A. Winkler

During a study of the adsorption of vapors and gases on porous powders with a Gulbransen type (1) torsion balance it was found that the instrument (at least the particular one available) lacked stability over a range of pressures and temperatures. A McBain–Bakr (2) quartz spiral balance had the necessary stability but had inadequate load capacity for a spiral with sufficient sensitivity. This note describes a null-point microbalance in which a torsion wire supports the load and the increase in weight during adsorption is determined with a highly sensitive quartz spiral.

A practically self-explanatory schematic diagram of the complete balance assembly is shown in Fig. 1. It has been found an advantage to have suitable

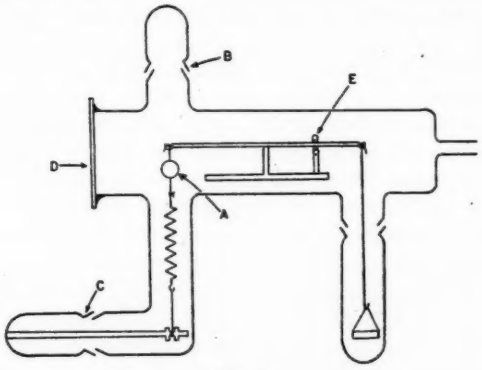

Fig. 1.

arrests (E) on the balance frame to limit the movement of the beam and thereby reduce the possibility of damage to the beam or the spiral. The quartz spiral is attached, as shown, from a hook on the counterpoise, A, at the opposite end of the beam from which the sample is suspended. Access to the balance may be had through B. The tension in the spiral is varied by winding or unwinding a very thin silk thread, which hangs from the lower end of the spiral, on a glass rod fitted through a ground glass joint C. Increase in weight during adsorption is determined from the extension of the spiral necessary to bring the beam to a null-point in the field of a microscope focused through the window D.

This type of balance has the calibration characteristics of the spiral‡

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†Graduate student, holder of National Research Council Studentship.

‡Quartz spirals are obtainable from: Houston Technical Laboratories, 2424 Branard Street, Houston 6, Texas, U.S.A.

employed. The balance used in this laboratory gave a linear weight–extension relation over at least 30 mm. extension of the spiral, in the temperature range −80°C. to 65°C. and the pressure range 10^{-4} mm. to atmospheric pressure, and the sensitivity was 0.163 ± 0.002 mgm./mm.

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THE VISCOSITIES OF AMMONIUM NITRATE SOLUTIONS AT 180°C.

BY A. N. CAMPBELL AND G. H. DEBUS*

Because of our interest in the Robinson–Stokes conductance equation (4), which requires a knowledge of the viscosity in order to calculate the equivalent conductance for any given concentration, we have determined the viscosities, at 180°C., of ammonium nitrate solutions ranging in concentration from 0.80% by weight up to 100% (molten salt). The conductances of these solutions had previously been determined in this laboratory (2). After obtaining the viscosities, however, we realized that not even a reasonable guess could be made at the value of Λ_0, the limiting conductance, at 180°. Elsewhere, we have made such guesses for temperatures of 35°, 95°, and even 110°C. (1) but the more the temperature is removed from 25°C., the only temperature at which Λ_0 is known experimentally, the greater the uncertainty. We therefore feel that our viscosity figures should be published at this time.

It is apparent that, if as much importance is attached to the Robinson–Stokes equation by others as by us, this must result in a stimulation of work in the dilute region at temperatures other than 25°C. The data might then be profitably treated by Stokes' simplified equation (3) to obtain Λ_0. A rigorous test of the Robinson–Stokes equation could then be made at temperatures other than 25°, since good data on conductances of concentrated solutions are beginning to accumulate.

EXPERIMENTAL

The method used has been described elsewhere (1). We express our results to the third decimal, the third decimal being uncertain. The viscosity is given as relative viscosity only, since the absolute viscosity of water is not known with great accuracy at 180.0°C.

RESULTS

The results are contained in Table I.

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TABLE I

VISCOSITIES OF AMMONIUM NITRATE SOLUTIONS AT 180.0°C.

No.	Wt. %	Density, gm./ml.*	Relative viscosity
1	0.80	0.892	1.011
2	8.51	0.928	1.093
3	16.06	0.957	1.168
4	23.97	0.993	1.268
5	32.06	1.030	1.395
6	38.68	1.061	1.524
7	45.24	1.099	1.715
8	50.19	1.121	1.862
9	54.89	1.145	2.055
10	58.59	1.166	2.237
11	61.96	1.184	2.397
12	69.70	1.225	2.819
13	76.50	1.272	3.34
14	84.07	1.322	3.98
15	88.63	1.356	4.65
16	100.00	1.44	10.1

**Calculated by interpolation of earlier results (2).*

1. CAMPBELL, A. N., DEBUS, G. H., and KARTZMARK, E. M. Can. J. Chem. 33: 1508. 1955.
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THE DETERMINATION OF HYDROGEN CHLORIDE IN TITANIUM TETRACHLORIDE*

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INTRODUCTION

Titanium tetrachloride, as prepared by the chlorination of titanium oxide in the presence of carbon, generally contains appreciable quantities of dissolved hydrogen chloride. The hydrogen chloride may form during the chlorination owing to the presence of moisture or hydrocarbons. Unlike the other impurities present (Cl_2, $COCl_2$, $VOCl_3$, $SiCl_4$, etc.) it is not completely eliminated during subsequent purification procedures. Also, since titanium tetrachloride is strongly hydroscopic, additional amounts of hydrogen chloride form and contaminate the product during handling in moist air.

When titanium tetrachloride is reduced to metallic titanium, the presence of HCl causes embrittlement of the metal due to hydrogen absorption. Hence,

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to control the embrittlement due to hydrogen, it is necessary to have a convenient analytical method for determining the amount of HCl dissolved in $TiCl_4$ and for following its removal by vacuum distillation. With the exception of an infrared spectroscopic determination recently published by the U.S. Bureau of Standards (1), little attention appears to have been given to this determination.

EXPERIMENTAL

Apparatus

Since the freezing points of HCl and $TiCl_4$ differ widely (−112°C. and −30°C. respectively), and since it was found that HCl was readily liberated from cold $TiCl_4$ solutions under vacuum, a method was developed to measure the pressure developed by a known volume of HCl liberated from $TiCl_4$ solutions. The apparatus is shown diagrammatically in Fig. 1.

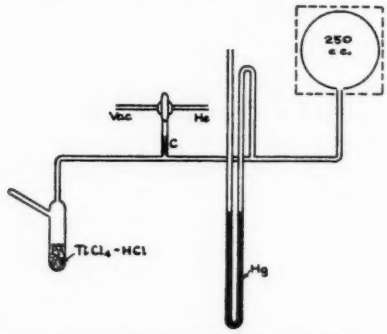

FIG. 1. Apparatus for determining HCl in $TiCl_4$.

The apparatus was constructed entirely of pyrex glass. Stopcocks were greased with Dow-Silicone stopcock grease. It was found that under the experimental conditions used in HCl determinations, no protection was required for the mercury in the manometer, or its alternative, a McLeod Gage. Volumes of all sections of the apparatus were determined before assembly by filling with water.

Procedure

The apparatus was thoroughly evacuated and flushed, using a mechanical pump and helium. With the apparatus at atmospheric pressure, an entry was blown into the $TiCl_4$ bulb and a specified (25.0 ml.) quantity of $TiCl_4$ admitted by pipette against a gentle countercurrent of helium. Helium was chosen because of its low condensation temperature. The apparatus was then resealed, the $TiCl_4$ sample frozen with liquid air, and the helium evacuated from the apparatus. As a precaution against attack of the stopcock grease by HCl, the capillary section C was then sealed, thus isolating the system.

When the liquid air was removed from the $TiCl_4$ container, the $TiCl_4$ melted slowly with a visible liberation of gas. When the $TiCl_4$ had melted completely, but had not been heated sufficiently to develop an appreciable

vapor pressure, it was refrozen with a slurry of CO_2 in a CCl_4–$CHCl_3$ mixture. This reduced the vapor pressure of $TiCl_4$ in the system to a very small value but did not alter the pressure developed by the HCl.

RESULTS

From the pressure of HCl developed in the system, and the known volume of the system, the quantity of HCl originally dissolved in the $TiCl_4$ was calculated assuming the Ideal Gas Law.

It was found that no change took place in the original pressure when the $TiCl_4$ was repeatedly refrozen and remelted. It was also shown that once a sample had been degassed by this procedure, the removal of HCl was virtually complete, as indicated by a zero HCl content when the determination was repeated on the same sample. Repeat determinations on previously degassed samples also showed that the helium used did not dissolve in or become mechanically trapped in the $TiCl_4$ during the determination.

Examination of the evolved gas with an infrared spectroscope has shown that HCl was the only constituent present.

The following results were obtained from triplicate samples of reagent grade $TiCl_4$:

Sample	% HCl
1	0.032%
2	0.034%
3	0.030%

When a sample of $TiCl_4$ at room temperature had been saturated with HCl at atmospheric pressure, it was found to contain 0.117% HCl.

CONCLUSIONS

The proposed method yields reproducible results for HCl within the range usually found in $TiCl_4$ (less than 0.1%).

1. JOHANNESEN, R. B., GORDON, C. L., STEWART, J. E., and GILCHRIST, R. J. Research Natl. Bur. Standards, 53: 4, 197. 1954.

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